

**University of Khartoum
Faculty of Engineering and Architecture
Department of Chemical Engineering**

**Utilization of Petroleum Coke as Alternative Fuel in
Cement Kilns**

A thesis Submitted in fulfillment of the requirements for the
degree of Master of Science in Chemical Engineering

By :

**Abd ElAzim Mohammed Ahmed ElAmrany
B.Sc Chemical Engineering**

Supervisor :

Dr. Bashir Mohammed El-Hassan

May 2005

ACKNOWLEDGEMENT

I would like to express my deep thanks and appreciations to Dr. Bashir Mohammed El- Hassan for his valuable advice and providing me valuable information in preparation of this study .

My thanks and gratitude extended to ostaz Hussain Ayoub computer lap. , for helping and cooperation .

I would like to thank ostaz El Tahir Bashir technician of central lab for helping in my experimental work .

I would like to thank Mr. Hamza Abd El- Moneim , plant manager in Atbara Cement factory for providing me valuable information .

Especial thanks to members of my family for encouraging and helping me .

ABSTRACT

In this study the feasibility of utilizing petroleum coke as alternative fuel in cement kilns was investigated . The study is a tempt to reduce cost of production in which the fuel represents more than 30 % because of the high price of fuel oil which ranges between 205 to 215 \$ compared with the price of petroleum coke between 40 to 50 \$ (FOB) .

The goal of the study is to optimize process control and alternative fuel consumption while maintaining clinker product quality .

The analysis of cost estimation is based on kiln No (3) in Atbara Cement Factory with a design capacity of 750 ton / day . The investigations included the evaluation of petcoke characteristics and advantages through physio – chemical and thermal treatment analysis for sample – 1 (Elsiwez Refinery – Egypt) and sample – 2 (Homs Refinery – Syria) .

Firing by petcoke required some modifications in the burning system and addition of pulverization mill , storage bunkers , and belt conveyors for grinding petcoke in powder to facilitate flowing through nozzle . The firing can be applied single or dual system to enable operating any of the two systems according to conditions available .

The results revealed that :

- The metal content in petcoke particularly vanadium and nickel if high causes hard burning and this may be overcome by fine grinding for petcoke .
- The high sulfur content of petcoke may cause operational problems in cement kilns , like blockage of cyclones and also environmental pollution by emissions thus it is necessary to add small dose of raw meal (limestone) to reduce sulfur . The study approved effectiveness in cost reduction when switched over from fuel oil to petcoke .

الخلاصة

215 205 %30

. (FOB) 50 40

(3)

750

-:

•

•

•

List of Content

		Page
	Acknowledgement	i
	Abstract (English)	ii
	Abstract (Arabic)	iii
	List of Contents	iv
	List of Tables	viii
	List of Figures	ix
	Abbreviations	x
CHAPTER I	INTRODUCTION AND OBJECTIVE	1
I-1	Introduction	1
I-2	Hypothesis	5
I-3	General Objective	5
I-4	Specific Objective	5
CHAPTER II	LITERATURE REVIEW	6
II-1	History of the delayed coking process	6
II-2	Coke formation , properties and structure	10
II-2-1	Crude oil origin	10
II-2-2	Parts of crude oil	11
II-2-3	Crude oil refining	12
II-2-4	Crude oil desalting	12
II-2-5	Atmospheric distillation	13
II-2-6	Vacuum distillation	13
II-2-7	Desalter influence on coke properties	16
II-2-8	Coke physical structure	17
II-2-9	Structure orientation in drum	25
II-2-10	Chemical property distribution	26
II-2-11	Overview of delayed coking process	30
II-2-12	Process description	31
II-2-13	Specific operating hazards	35
II-2-14	Controlling the hazards	41
II-2-15	Specific operation hazards	42
II-2-16	Emergency evacuation – preparation and procedures	47
II-2-17	Toxic exposures , dust irritants and burn truma	48
II-3	Modern delayed coking process	49
II-4	Delayed coking drum cycle	49
II-4-1	Drum warm – up (vapor heat)	51
II-4-2	On – line filling	51
II-4-3	Steam – stripping / hot spots	52

II-4-4	Water cooling / drum bulging	53
II-5	Delayed coking unit hardware	55
II-5-1	Feed preheat	56
II-5-2	Coker charge pumps	56
II-6	Coker tube furnace	57
II-6-1	Coker furnace design	57
II-6-2	Heater tube decoking	59
II-6-3	Steam spalling	59
II-6-4	Steam – air decoking and pigging	60
II-6-5	Heater tube deposits	61
II-7	Transfer line and switch valve	61
II-7-1	Transfer line	61
II-7-2	Switch valve	62
II-8	Coke drums	62
II-9	Over head vapor lines	63
II-10	Antifoam injection system	64
II-11	Coker fractionator	65
II-12	Hydraulic coke cutting system	66
II-12-1	Cut water pump	66
II-12-2	Cutting equipment	67
II-12-3	Coke cutting technique	67
II-13	Review of Fluid coking and Flexicoking technology	68
II-14	Historical perspective	70
II-15	Process description	72
II-15-1	Fluid coking	73
II-15-2	Flexicoking	77
II-16	Products – yields , qualities and dispositions	80
II-16-1	Reactor gas	81
II-16-2	Coker naphtha	82
II-16-3	Coker gas oil	82
II-16-4	Bottoms	83
II-16-5	Product coke	83
II-16-6	Low BTU gas	85
II-17	Material Balance	86
II-18	Process selection criteria	88
II-18-1	Continuous process	88
II-18-2	Feed and operations flexibility	89
II-18-3	Reliability	90
II-18-4	Train capacity /size	92
II-18-5	Environmental	92
II-18-6	Economic comparison	93

II-19	Scanning Electron Microscope	95
II-20	Kiln system chemistry	99
II-21	Process energy requirements	101
II-22	Fuel oil to coke switch over	102
II-22-1	Facilities and equipments requirements	102
II-22-2	Operational consequences of switch over	103
II-23	Air pollution , sources , impacts and standards	104
II-24	Emission sources	104
II-25	Environmental impacts of principal air pollutants	105
II-26	Emission standards	107
II-27	Stack emission from kiln system	108
II-28	Kiln emission flows	109
II-29	Particulate Matter	901
II-30	Oxides of sulfur (SO _x)	111
II-31	Oxides of nitrogen (NO _x)	112
II-32	Carbon monoxide (CO)	115
II-33	Volatile Organic	116
II-34	Emission of volatile organic compounds	116
II-35	Stack Emission from coke pulverization mill	116
II-36	Spontaneous coke fires	118
II-37	Coke dust explosions	119
II-38	Coke dust impacts on electrical system	121
II-39	Contamination of soil and ground water	121
II-40	Noise	121
II-41	Pollution control measures	121
II-41-1	Process control optimization for emission control	121
II-41-2	Particulate Matter emissions control	123
II-41-3	Control of PM emissions from kiln and coke pulverization mills	123
II-41-4	So _x emissions control	126
II-41-5	Wet scrubber	126
II-41-6	Activated carbon adsorption	127
II-41-7	NO _x emissions control	127
CHAPTER III	MATERIALS AND METHODS	128
III-1	Materials	128
III-1-1	Petroleum coke	128
III-1-2	Lime stone	128
III-2	Method	128
III-2-1	Screen analysis of petroleum coke	128
III-2-2	Determination of sulfur in petcoke	128

III-2-3	Plotting of the results	130
CHAPTER IV	RESULTS AND DISCUSSION	131
IV-1	Screen analysis of petroleum coke	131
IV-2	Effect of particle Size on percentage Weight	132
IV-3	Effect of Particle Size on percentage cumulative weight	134
IV-4	Effect of particle size on percentage Ash content	136
IV-5	CaSO ₄ formation during petcoke burning	138
IV-6	Addition of lime stone to petcoke – sample - 1	139
IV-7	Effect of temperature on sulfur removal	141
IV-8	Effect of particle size on removal of sulfur	143
IV-9	Thermal treatment of sample -2	145
IV-10	Effect of particle size on percentage cumulative weight passed	146
IV-11	Effect of particle size on percentage weight passed	148
IV-12	Effect of particle size on percentage Ash content	152
IV-13	Addition of lime stone to petcoke – sample - 2	152
IV-14	Effect of particle Size on removal of Sulfur	154
IV-15	Impact on production costs	157
IV-16	Basis of analysis	157
IV-16-1	Annual production	157
IV-16-2	Capital investment	157
IV-17	Effect of operational costs	158
IV-18	Technical data (offer received from pillard company – France	164
CHAPTER V	CONCLUSION AND RECOMMENDATIONS	171
V-1	Conclusion	171
V-2	Recommendations	173
	Bibliography	175
	Appendices	178

List of Tables

Table No.		Page
II-2-9-1	Coke CTE by Orientation	26
II-2-1	Property Distribution in the Coke Drum	28
II-2-2	Typical Properties of Delayed Petroleum coke	28
II-2-3	Advantages and Disadvantages of petroleum coke	29
II-4	Typical short cycle coking operations	50
II-13-1	Rejections of contaminants by thermal conversion processing .	69
II-16	Product Yield	81
II-16-5-1	Green Coke Property Comparison	84
II-27-1	Fuel Energy Requirements of cement kiln	101
II-31-1	Impact of Air Pollutants on Environment and Human Health & Life	106
II-32-1	Ranges of standard applicable to the cement production plant in different European countries .	107
II-35-1	Particulate matter emission factors in Kg per ton clinker .	110
II-36-1	Uncontrolled SO _x emission factors in Kg per ton of clinker .	112
II-37-1	Uncontrolled NO _x emission factors in Kg per ton of clinker .	114
II-38-1	Uncontrolled CO emission factors in Kg per ton of clinker .	115
II-41-1	Coke pulverization mill stack (with fabric filter) – cement plant – Pakistan .	117
IV-17-1	Differences in unit costs of production (in \$ per ton cement on account of fuel Switch – over from fuel Oil to petcoke .	163

List of Figures

Fig. No.		Page
II-2-1	Basic Refinery	14
11-2-2	Flow Process in general conversion refinery	15
11-2-12-1	Delayed coker unit cutaway to depeicit drum in filling and migrate mode (left) and drum in cutting mode (right)	33
11-2-12-2	Delayed coker unit – coke drum and hydroblast system	34
11-5-1	Basic Coker Operation	55
II-15-1-1	Fluid Coking	74
II-15-2-1	Flexicoking	79
II-17-1	Product Dispositions from Fluid Coking	86
II-18-3-1	Run Length History for Fluid Coking and Flexicoking	91
II-19-1	SEM photo showing a distribution of sulfur particles on the matrix of petroleum coke (before treatment)	96
II-19-2	SEM photo showing a petroleum coke particles of sample treated at 1000 °C.	97
II- 19-3	SEM photo showing some particles of sulfur on matrix of petroleum coke .	98
II-20-1	Schematic illustration of sulfur circulation	100
IV-2-1	Particle Size vs Weight passed, % (Sample -1- Elsiwez Refinery – Egypt)	133
IV-3-1	Cumulative weight vs particle Size (Sample -1 – Elsiwez Refinery – Egypt)	135
IV-4-1	Particle Size vs % Ash Content (Sample -1- Elsiwez Refinery – Egypt) .	137
IV-7-1	Temperature vs % Sulfur Removal (Sample -1 – Elsiwez Refinery – Egypt)	142
IV-8-1	Particle Size vs % Sulfur Removal (Sample -1 Elsiwez Refinery – Egypt)	144
IV-10-1	Particle Size vs % Cumulative weight (Sample -2- Homs Refinery – Syria) .	147
IV-11-1	Particle Size vs % weight passed (Sample -2 –Homs Refinery – Syria) .	149
IV-12-1	Particle Size vs % Ash content (Sample -2 – Homs – Refinery – Syria)	151
IV-13-1	Temperature vs % Sulfur Removal (Sample -2 Homs Refinery – Syria) .	153
IV-14-1	Particle Size vs % Sulfur Removal (Sample 2– Syria) .	155

Abbreviations

EAF	Electric Arc Furnace
VRC	Vacuum Reduced Crude
HCGO	Heavy Coker Gas Oil
DCU	Delayed Coking Unit
FCC	Fluid Catalytic Cracking
NEQS	National Enviromental Quality Standard
PH	Pre – heater
PC	Pre – calciner
AC	Activated Carbon
ES	Electrostatic Precipitator
VM	Volatile Matter
VOM	Volatile Organic Matter
PM	Particulate Matter
PF	Pulverized Fuel
CTE	Coeffecient of Thermal Expansion
www II	World War II
OSHA	Occupational Safety and Health Administration (USA)
FF	Fabric Filter
FOB	Free On Board
C & F	Cost and Freight
BTU	British Thermal Unit
SEM	Scanning Electron Microscope
RPM	Revolutioon Per Minute
GPCS	Gulf Petroleum Company (Sudan)

CHAPTER 1

INTRODUCTION AND OBJECTIVE

I-1 Introduction :

Coking is a thermal cracking operation that converts residual from the bottom of the vacuum distillation unit into coke and gas oil.

It is slow operation that allows the thermal reactions to go to completion.

There are three types of coking process

- 1- Delayed Coking .
- 2- Fluid Coking .
- 3- Flexicoking .

Delayed coking is a thermal cracking process used in petroleum refineries to upgrade and convert petroleum residuum (bottom from atmospheric and vacuum distillation of crude oil) into liquid and gas product stream, leaving behind a solid concentration carbon material, petroleum coke.

Secondary fuels have proved to be one of the main alternatives in the effort to reduce fuel consumption . Petroleum coke especially has constituted a challenge for industry . The main reason is its low price and its high availability due to the fact that petcoke is a by- product from oil refineries .

Cement industries are striving to lower their production cost, one effective method of which is the substitution of traditional fuels such as coals, oil and natural gas with petcoke.

Its high sulfur content can present operational difficulties if not properly addressed.

The main difficulty in burning petcoke is its low reactivity due to low volatile content. This low reactivity can be compensated for in a number of ways, such as finer grinding, high momentum rotary kiln burner design and calciner design.

The sulfur content of the product is a function of the sulfur content of the feed, yield of coke, and source of crude.

Sulfur is present in coal in three forms, as organic sulfur, as pyritic sulfur(Fe S_2), and as sulfates. This study is concerned with suggestions to avoid operational problems of high sulfur content of petcoke when it is used as an alternative fuel in cement kiln or power generation.

Process engineering research aims primarily at optimizing the energy consumption and use of manpower in cement manufacture as well as the quality and uniformity of the cement, and at minimizing emissions.

Petroleum coke, a by-product from the oil refining industry, has a high calorific value, but a low volatile

content and normally higher levels of sulfur and nitrogen than traditional fuels . While oil refineries consider it a waste product, to the cement manufacturer it represents an economical fuel alternative.

Lower costs and special precautions using petcoke as primary fuel source can substantially lower production cost. Besides the high calorific value that makes petcoke ideal for firing in a cement.

When changing to petcoke , however , special precautions need to be taken as the low volatile and high sulfur nitrogen contents may cause operational problems in terms of :

- Blockage in the preheater cyclones.
- Built – ups in the riser ducts.
- Higher SO₂, NO_x and CO emissions.
- Dusty Kiln.
- Unstable Calciner operation.

World petroleum coke output has grown by 4% Pa since 1991 and could rise from 83 Mt (including 59 Mt marketable) in 2001 to 88 Mt by the end of 2005. This figure could be exceeded as 13.5 Mtpy of new or expanded capacity could come on stream during this period.

Growth in North America (3.3Pa) and Europe (1.4 % Pa) is below the world average but this is balanced significant expansion in Asia (about 8% Pa).

World demand for petroleum coke is expected to rise mainly due to increasing oil production and consumption decreasing quality of crude oil feedstock, and higher demand for gasoline and other transportation feeds. The progressively stringent environmental regulations for these fuels will lead to a greater need for coking.

Globally, around 75% of petroleum coke output is burned as a fuel, in North America around 90 % of coke used in the energy sector is catalyst coke that is burned as a fuel in host refineries . In Europe and the pacific region, non- energy applications (including electrodes and cement manufacture) are proportionally more important. The manufacture of carbon and graphite electrodes is the largest non- fuel end use for petroleum coke. The petroleum coke is the main ingredient in carbon anodes for primary aluminum smelting and graphite electrodes for steel production Via the electric arc furnace (EAF) process .

I-2 Hypothesis :

Utilization of petcoke with high sulfur content is not economical as some operational problems may appear and the maintenance cost is adversely affected .

1-3 General objective :

To assess the effectiveness of utilizing petcoke as alternative fuel for cost reduction in cement kilns .

I-4 Specific objective :

- i) To evaluate method suggested for reducing sulfur in petcoke .
- ii) To identify operational problems if any and how to overcome it , when utilizing petcoke as a fuel in cement kilns .
- iii) To determine the effect of temperature and particle size in sulfur removal of petcoke .
- iv) To determine cost effectiveness .

CHAPTER II

LITERATURE REVIEW

II-1 History of the delayed coking process :

Petroleum coke was first made by the pioneer oil refineries in northwestern pennnsylvania in the 1860,s . These primitive refineries boiled oil in small , iron stills to recover kerosene , a valuable and much needed luminescent . The stills were heated by wood or coal fires built underneath which over- heated and coked the oil near the bottom . After the distillation was completed, the still was allowed to cool so the workmen could

dig out the coke and tar before the next run .(conner 1981) . The use of single horizontal shell stills for distillation of the crude was used until the 1880,s with the process sometimes stopped before bottoms coked to produce a heavy lubricating oil . Multiple stills were used to process more fractions by running the stills in series with the first still producing the coke . In the 1920,s the tube furnace with distillation column (bubble cap distillation trays patented by Koch ushered in the modern distillation column) were being built with the bottoms from the distillation column going to wrought iron stills in which the total outside of the horizontal still was in direct contact with the flue gases . This produced the maximum amount of heavy gas oil . Some of these units were still in operation after World War II . Operators assigned as decokers used picks , shovels , and wheel barrows and had rags wrapped around their heads to protect against the heat .

The coke that was produced in the horizontal stills had a high density, low volatile matter (VM) content of around 8 wt %, and less than 1 wt % moisture . One problem was faced that ash content was high , around 1 wt % compared to under 0.2 wt % in most modern delayed cokers . Conners 1981 thought that this was due to the lack of desalting and washing of the crude oils processed at that time .

The origin of the vertical coke drum was probably from thermal cracking of gas oil for the production of gasoline and diesel fuel . From 1912 to 1935 the Burton process developed by standard oil at whiting , Indiana converted gas oil to gasoline with the production of petroleum coke . Dubbs and other thermal cracking processes also produced petroleum coke . Lack of an adequate supply of crude oil and the lack of a heavy oil market caused landed – locked middle American refineries to process the heavy fuel oil (atmospheric distillation bottom and vacuum distillation bottom) in a delayed coker to produce more gasoline and diesel fuel . Decoking the drums was difficult . “ Manual decoking was a hot and dirty job various mechanical device were tried . One of the common systems employed was to wind several thousand feet of steel cable on holding devices in the drum The cable was pulled by a winch , to loosen the coke . Coke was also removed by drilling a small hole , then a large hole , after which beater balls on a rotating stem knocked out the remaining coke .

The first delayed coker was built by standard oil of Indiana at whiting,Indiana in 1929 (Gamson 1983) . The development of hydraulic decoking in the late 1930,s

Shell oil at wood River , Illinois presented a paper on hydraulic decoking 4.0 m (13 ft) diameter Dubbs units and stated that they had patents along with Wrthington pump

company on hydraulic decoking bits and nozzles (Court 1938) . Standard oil of Indiana had patents on the original cutting nozzles used by pacific pump (Porton 1998) . A very similar nozzle is currently used in the new compact combination coke cutting unit . A pilot hole is drilled down through the coke drum using high pressure water , and then the coke is cut out with a drilling bit with horizontal water nozzle . Roy Diwoky while at standard oil whiting was one of the key people in developing the hydraulic decoking in the 1930,s .

Diwoky in may 1952, while executive vice president of pan Am southern corp.(owned by standard oil of Indiana), worked with Great Lakes Carbon Corporation to produce the first needle coke in a delayed coker . Bernard Gamson, the Director of Research and development for Grate Lakes Carbon at the time, stated in a report that Diwoky was “ the father of delayed coking” (Peters 1983).

Delayed coking combined a number of the features and improvement from the development of the thermal cracking process . The use of pressure as well as heat for cracking and separating the heater from the coker and the use of two drums enabled the delayed coker to operate on a continuous basis .

The number of cokers built before 1955 was small , with a surge in delayed coker construction between 1955 to 1975 at 6% per year and an 11% growth rate during 1965 to1970 period (Conners1981) . The growth of delayed cokers was in step with

the growth of fluid catalytic cracking and rapid decline in thermal cracking . A fluid coker , similar to a fluid cracker except that fluid coke is circulated instead of catalyst, was first built in 1045 at Billings, Montana. Five more fluid cokers were built in late fifties, and one in 1970.

In 1958, the head of petroleum refining engineering at Colorado School of Mines, J.O. Ball, stated that there would not be any more delayed cokers built.

Ball thought all new cokers would be fluid cokers , and that a delayed coker was just a garbage can in the refinery .

Today there are 49 operating delayed cokers in the U.S and only six fluid cokers/ flexicokers .

II-2 Coke formation , properties and structure :

II-2-1 Crude oil origin :

In order to understand the components of petroleum coke , we must review the origin of the vacuum reduced crude (coker feed) and crude oil from which it originates . The formation of crude oil

is thought to be derived from ancient remains of animals and plants. The organic matter was squeezed out of the strata probably by the connate water or water that was originally in formation . Ancient stream beds , reefs , and sand beaches had the porosity to allow migration of the oil water and provided a conduit for this oil and water material to flow. The final requirement is a trap for the oil . Oil is not in an open pool but

is trapped between layers of sand or in cracks of limestone . The basic trap is the anticline where the formations were pushed up into a dome shaped area where the oil and gas accumulated . Also , faulting of geologic formations pushed oil up against some impervious formations forming fault traps. The salt domes in the Gulf Coast of the United States have been a big producer of oil .

Spindletop near Beaumont , Texas was a prime example. Salt laid down in the bottom of a drying sea , and these formations were covered by over five miles of sediment . The resultant pressure liquified the salt which then started to migrate towards the surface .

The geologic formations are pushed up as the salt plug punches through the formations . The salt , being impervious to the oil, forms an excellent trap .

The vanadium and nickel are in the crude oil as porphyrins or metal chelates . Originally the metals were probably magnesium (chloroph II) and iron (hemoglobin) .

The ratio of the metals to each other is due to when and how they were byed . Some of the vanadium and nickel can be loosely held between the asphaltene molecules (intercalation) . The other metals are complexed onto the water droplets and probably were due to the structure that the oil migrated through . Crude oils such as the paraffinic Pennsylvanian crude contain very small amounts of asphaltenes . It is possible that the

asphaltenes dropped out of the oil phase but are still down in the formation .

II-2-2 Parts of crude oil :

Crude oil contains three different fractions . The “ oil” is the hydrocarbon : paraffinic , naphthenic, and aromatic which also

contain sulfur and nitrogen . The second part of the crude oil , the resins, coat the asphaltene fraction so that it can be peptized into the crude oil . The resins are brown , sticky hydrocarbon which contain nitrogen , oxygen , and sulfur , are soluble in n-pentane but insoluble in propane and have molecular weight greater than 3000 .

The asphaltenes contain the chelated metals , vanadium, nickel, and possibly some calcium along with sulfur, oxygen, and nitrogen. During crude oil distillation, the asphaltenes are not volatilized and remain in the vacuum reduced crude along with most of the resin fraction .

Jakob (1971) thought all the resins and the asphaltenes dropped out in the coker and the remaining coke was made from the oil fraction . With higher temperatures and lower pressures, the hydrocarbon part of the coke could be reduced but not the resin and asphaltene fraction . The amount of coke produced in a delayed coker is always more than the corradson or Ramsbottom carbon residue percentage by a factor of about 1.6

II-2-3 Crude oil refining :

To understand the delayed coking process, one must understand how the delayed coker is integrated with the rest of the refinery . Delayed coker feed originates from the crude oil supplied to the refinery. Therefore brief descriptions each of the processing steps preceding the delayed coking unit are provided below . A basic refinery flow diagram is shown in figure II-2-1 .

II-2-4 Crude oil desalting :

Crude oil contains around 0.2 % water in which is mixed soluble salts such as sodium chloride and other metals which are on the edge of the sphere of water. In desalting , crude oil is washed with around 5% water to remove the salts and dirt from the crude oil . The water being heavier than the oil , drops out of the bottom , and the cleaned oil flows overhead with around 0.1 % water .

II-2-5 Atmospheric distillation :

The desalted crude oil is heated in a tube furnace to over 385°C (725 °F), just below the temperature that cracking of the oil can occur , then flashed into a distillation column . The primary products are straight run gasoline, kerosene , jet fuel ,diesel , atmospheric gas oil (AGO) and atmospheric reduced crude .

II-2-6 Vacuum distillation :

The atmospheric reduced crude (ARC) is heated to around 395°C (743 °F) and flashed into a vacuum distillation column

that is operated at low pressure , 10 mm Hg absolute desired but more common 25 to 100 mm Hg absolute . The desired aim is to lift the maximum amount of oil boiling below 565 °C into heavy vacuum gas oil (HVGO) reducing the production of vacuum reduced crude (VRC) , the main feedstock to the delayed coker . The HVGO and the AGO are the principal feedstocks to a fluid catalytic cracking unit (FCCU) for the production of gasoline and diesel .

Improving vacuum distillation is one of the best methods for increasing gas oil yield in a refinery while at the same time reducing the amount of vacuum reduced crude (coker feed) . This enables higher refinery throughput rates to be achieved .

reducing the amount of vacuum reduced crude (coker feed). This enables higher refinery throughput rates to be achieved.

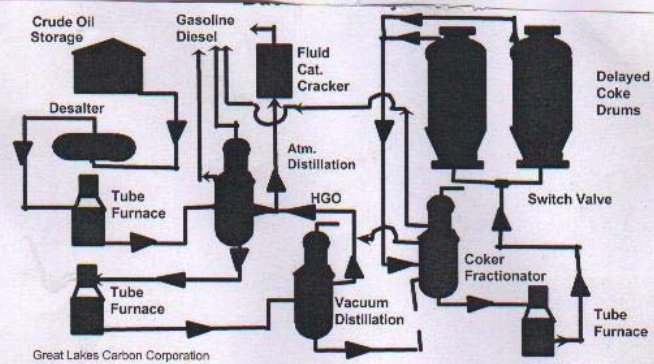


Figure II-2-1 BASIC REFINERY

Source : Gamson , (1983) .

Figure II-2-1 BASIC REFINERY

Source : Gamson , (1983) .

**Figure II-2-2 FLOW PROCESS IN GENERAL
CONVERSION
REFINERY**

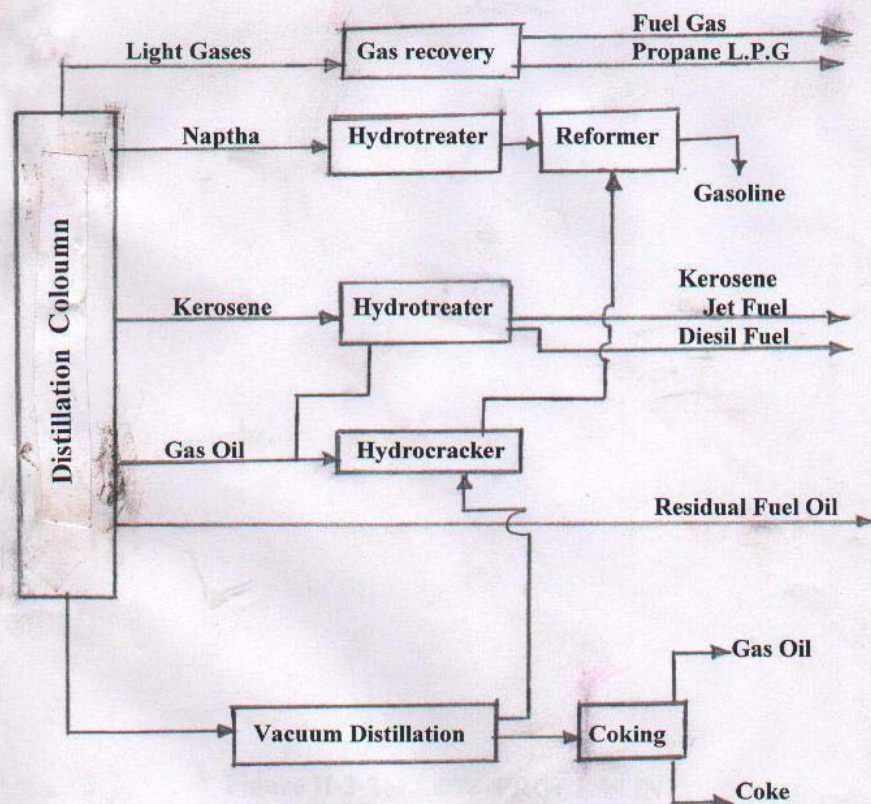


Figure II-2-2 Flow Process In General Conversion Refinery

Source : Gamson , 1983 .

Source: Gamson , (1983) .

II-2-7 Desalter's influence on coke properties :

The crude oil desalter is one of the critical pieces of equipment in refinery for producing good quality anode grade coke (coke low in metals suitable for calcination and use in the aluminum industry) and keeping a coker furnace on line . Crude oil contains around 0.2 % water in which is mixed the soluble salts such as sodium chloride and other metals which are on the edge of the sphere of water . In desalting , the crude oil is washed with 5 % water to remove the salts and dirt from the crude oil . The water being heavier than oil , drops out of the bottom , and the cleaned oil flows overhead with around 0.1 % water .

Whithout good desalting , caustic (sodium hydroxide) or filming amines must be added to eliminate the chloride corrosion in the overheads of the distillation and vacuum distillation lines . The chlorides are usually in the form of salt (sodium , calcium , and magnesium chloride) . The salt content can vary from 50 to 300 lbs per 1000 barrels of crude . Since the number of droplets are high , around 9×10^{11} , the amount of dirt and other_metals on_the outside of these water droplets is appreciable . The magnesium chloride causes most of the corrosion since it brakes down at low_temperatures in the distillation column liberating chlorine which forms hydrochloric

acid that attacks the overhead lines in both the vacuum and atmospheric distillation units .

Sodium is a catalyst for burning of carbon (air and carboxyl reactivity in backed anodes) and also causes rapid tube fouling in the coker tube furnace . The mechanism for rapid fouling of tubes due to sodium is not fully understood , but it is known that if the tubes are not water washed after steam – air decoking to remove the crystals of salts, the unit will rapidly foul . Iron in fine particles, probably iron sulfide , is very difficult to remove in a desalter , but some chemical companies can do a better job than others . Metals that the desalter does not remove will end up in the coker feed and ultimately in the delayed coke .

II-2-8 Coke physical structure :

- Coefficient of Thermal Expansion:

To determine a quantitative value describing coke structure, the coke is calcined , ground to flour , mixed coal tar bitch, extruded to orientate particles into 13 mm rods , baked to 850 °C, and graphitized to 2900 °C , and then the difference in expansion at 0 °C and 50 °C is measured for coefficient of thermal expansion (CTE) determination .

Typical values of CTE corresponding to coke structure are: needle coke (acicular) , 0 to 4 , sponge coke , 8 to 18 , and shot coke (isotropic) , >20 (cm / cm / C°x10⁻⁷).

i- Shot coke :

The production of shot coke in delayed coker requires high concentrations of asphaltenes in the feedstock , dynamics (velocity and/or turbulence) in the coke drum , and high coke drum temperatures. A coker feedstock high in oxygen content can also produce shot coke . When asphaltene content compared to Conradson carbon residue content of the coker feed is high , the production of shot coke is very likely. The present trend in refineries is to run heavier crudes with higher asphaltene contents and to improve operation of the vacuum distillation unit to produce a heavier VRC with a higher asphaltene content . This trend towards increased production of shot coke has been observed in refineries which originally ran atmospheric reduced crude in the delayed coker , never making shot coke after vacuum distillation unit was installed .

Shot coke is produced as the oil flows into the coke drum . With the light ends flashing off , small globules of heavy tar are suspended in the flow . These tar balls rapidly coke due to the exothermic heat produced by asphaltene polymerization . (cokers going from spong coke production to shot coke

production have seen the drum overhead temperature increase by as much as 30 °C)

The balls then fall back into the drum as discrete little spheres two to five millimeters in size . In the main channel up through the

drum , some of the spheres will roll around and stick together forming large balls as large as 25 centimeter .

When these large balls are broken , they are found to be composed of many of the two to five millimeter size balls . Normally , small shot coke balls from different delayed coker s will be nearly the same size , however , Mexican Mayan VRC has been found to produce larger shot coke balls upon delayed coking than does Venezuelan VRC . It is thought that smaller balls are made when very high feed rates are used in the coker .

Aromatic feeds, such as decant oil from the FCCU, can help eliminate shot coke formation . All other methods of eliminating shot coke such as decreasing temperature ,increasing drum pressure, and increasing recycle ratio , will all increase coke yield (decrease more valuable liquid yields) which is not desired .

It is very difficult to produce shot coke spheres in pilot delayed coker . Spherical shot coke can only be produced in pilot delayed cokers if the velocity in the drum and the temperature in the drum both very high . In a batch (pot) coker , the typical spherical form of shot coke cannot be produced at all

, but the shot coke does have a high CTE value similar to the spherical form .

Shot coke is unique in that the small spheres two to five in diameter each have a slick shiny exterior coating of needle or a circular type carbon . The inside of each sphere contains isotropic

or amorphous type coke as originally described by March and Bacha(1984) . Shot coke cannot be used in making aluminum anodes because the outer needle coke layer of the shot spheres has a very low coefficient of thermal expansion while the inside of the sphere , being isotropic , has a very high coefficient of thermal expansion .

When rapidly heated in a calcium kiln , the outer layer is cracked and pulled away from the center , thus when used in an anode with a coal tar binder , the binder adheres to the outer layer (egg shell). This results in many cracks between the ball and the skin causing the anode to crack and dust in an aluminum smelter cell, (Ellis 1993) .

ii- Spong coke :

Sponge coke is named for its sponge – like appearance and is produced from VRC with a low to moderate asphaltene concentration . If a sponge coke meets strict proper specifications it is considered anode grade sponge coke suitable for calcination for use in making carbon anodes for the aluminum industry.

Otherwise , if sponge coke meets the more lenient fuel grade specifications, it can be used in its raw form for fuel .

The biggest problem for refineries producing anode grade sponge coke is obtaining the low volatile matter (VM) required . The metals and sulfur are strictly controlled by the crude being processed , but the VM is in the control of the delayed coker operators . Temperature in the drum is the most critical item , along with cycle time at temperature helps to decrease the VM.

Increased recycle can increase the temperature in the drum . Insulation of the transfe line and coke drum , especially the upper sections of the coke drum , are critical for obtaining low VM coke . Poor insulation and other bad practices on the delayed coker require higher temperature in the tube furnace , which results in shorter campaigns and more down time for decoking of the furnace

Monitoring the seal steam to prevent decreasing the temperature in

the transfe line , elimination of seal oil on the pressure relief devices on the transfe line , and minimizing the amount of carrier oil for the antifoam all help in increasing the temperature in the drum in order to decrease VM of the resultant coke .

Raw or “ green” sponge coke must be calcined before it can be used in making anodes . The density of the calcined coke is critical for producing good carbon anodes . The higher density , the more carbon can be incorporated into the anodes ,

and the longer the anode will last . Vibrated bulk density (VBD) of the calcined coke must be greater than 86 (grams / 100 CC) . The best single property that correlates from the raw coke is the Hardgrove

Grindability Index (HGI) . Raw coke with lower than 70 HGI usually can be calcined to produce an 86 VBD .

Volatile matter is another good property used to correlate how well the raw coke will calcine . Structure is a strong factor in calcinability also , since cokes with low CTE must have volatile much lower than a more isotropic type coke to produce the same density. Porosity of the calcined coke should be low and is also a function of the raw coke volatile matter . The ash in the calcined coke normally around 0.2 % with vanadium and nickel combination under 500 ppm . Sodium and calcium are very strong catalysts for air burn of an anode . Vanadium , nickel and iron and other metals causes increased carboxyl reaction in the bottom of the anode . The sulfur in the anode must be below 3.5 % to prevent the sulfur from increasing the electrical resistance of the cast iron connection between the anode and the power rod .

Normally , sulfur is more of an environmental and scrubbing problem . Sulfur can cause the real density of calcined coke to decrease due to an increase of the porosity and micro cracking of the calcined coke . Sulfur does help reduce

reactivity (air and carboxyl) by reacting with the caustics which are strong catalyst .

Aluminum production requires around one – half kilogram of carbon per kilogram of aluminum produced .
Anode grade coke

aluminum cell is being scrubbed with the alumina used as feed to the aluminum cells . Therefore, any metals in the coke would get into the alumina and into the aluminum metal produced . The carbon is used in the aluminum smelter as a means of carrying electrical power into the cell . It takes around 15 KW of power per Kg of aluminum produced . A carbon with some porosity must be used since gases coming off the cell would block corrosive fluoride salts used in the aluminum cell and the problem with the evolution of the gases makes the discovery of a non- consumable anode difficult .

iii- Needle coke :

Needle coke , named for its needle – like structure , is produced from feedstocks without asphaltenes present normally FCCU decant oils . Needle coke is the premier coke , used in graphite electrode manufacturing (used in steel arc furnaces) , but needle coke require special feedstocks , special coking , and special calcination to obtain the optimum properties . The Shea patenten on needle coke gives an accurate description of the formation of needle coke , still relevant today.

Most needle coke is produced from hydrodesulfurization decant oil (due to low sulfur requirement for non- puffing coke , that can be nearly flash graphitized in the new direct current (DC) length – wise graphitization method , without splitting the electrode) . The principle requirement for needle coke is that the CTE must be 2.0 or below (low CTE is required to prevent spalling due to the thermal stresses on the tip of the electrode which can be as high as $2000\text{ }^{\circ}\text{C} / \text{cm}$) . Needle coke must have low sulfur ($0.6\text{ wt } \%$) and nitrogen contents in order to non- puffing during graphitization to $2900\text{ }^{\circ}\text{C}$ (measured by a special dynamic puffing test that is proprietary) . Needle coke must also have a maximum amount of coarse sizing ($>6\text{ mm}$) , a minimum amount of fines ($< 1\text{ mm}$) ,good density ($>78\text{ gm} / 100\text{ cm}^3$, 4/6 mesh test) , low ash content ($< 0.3\text{ } \%$, any ash leaves a void when graphitized) , and a high real density ($2.13\text{ gm} / \text{cm}^3$) .

Even with all the property specifications , an electrode manufacturer will not accept a calcined needle coke for production until they have actually run a trial lot through the plant and trials on the electric arc furnace . Most graphite plants want a needle coke with low variability so that they can set up the optimum pitch level , extruding and backing to produce a good electrode . The most popular electrode

furnace is the 24 inch (60 cm) , with a demand for larger than 30 inch

(76 cm) , for DC single electrode furnace . Obtaining good needle coke is still a black art for excellent graphite electrodes. The principal property that the electric arc steel mill wants in a graphite electrode is a low amount of graphite per ton of steel melted . In single electrode DC furnaces , the amount of graphite per ton is below 2 Kg /ton. With better practices and foamy slag , AC furnaces (using three electrodes due to three – phase electric power) have approached this level.

II-2-9 Structure orientation in drum :

Samples of coke cut both vertically and horizontally showed that the coke was oriented in the drum . The coefficient of thermal expansion is much lower in the vertical direction compared to horizontal , 132 % lower in the raw coke , 505 % lower in the calcined , and 285 % lower in the graphitized sample .

Gas bubbles , formed from cracking , migrate upward during coke formation in the liquid , orientating the mesophase chain growth .

Table II-2-9-1 Coke CTE by orientation :

CTE (cm/cm/°C x10 ⁻⁷)	<u>vertical</u>	<u>horizontal</u>
Raw Coke	117	154
Calcined 850 °C	1.8	9.1
Graphitized 2900 °C	0.2	5.7

Source: Hardin ,1992

II-2-10 Chemical property distribution :

The ash is mainly in the lower sections of the coke drum with a high percentage in and near the channels up through the coker . The ash being a particulate drops out of the oil , or the wall of the channel traps out the particles , otherwise known as the fly paper effect .

A cross- section of the coke in the drum was cut into small cubes which were analyzed for ash content . The ash level was five to ten fold higher near the channels compared to the rest of the section . In an experiment where a paint pigment sized chromium oxide was pumped through the tube furnace into the coke drum in an attempt to get good dispersion in the coke (chromium oxide is a puffing inhibitor in needle coke) , all the chromium oxide dropped out in one

spot in the lower section of the coke drum up about six inches from the inlet . This is normally the first spot where the main channel starts to branch. Several runs were made with identical results . Injecting the pigment through the top of the drum distributed the material uniformly in the coke , indicating that there is some back mixing in the top of the drum either in the froth layer or in the liquid .

Iron , silicon , and ash are in the coke as particulates . These metals concentrate in the lower section of the coke drum as shown in Table II-2-1. Vanadium and nickel are in crude oil as metal chelates or porphyrins in the asphaltene fraction . It was puzzling that vanadium and nickel are not uniformly distributed in the drum until it was understood that some of the metals are intercalated in the structure and are not chemically bonded , so they drop out early in the coke drum similar to the ash and particulates . Volatile matter (VM) in the coke drum is normally high in the top of the drum due to the short residence time of the material .

The sulfur is uniformly distributed in the drum unless the feedstock to the drum is changing as the drum is filled . (Hardin 1992) .

Table II-2-1 Property distribution in the coke drum – wppm :

<u>Bottom</u>	<u>Top</u>	<u>Middle</u>
Iron	40	440
1300		
Silicon	60	150
380		
Ash	1000	2100
4500		
Vanadium	267	310
380		
Nickel	130	160
230		
VM (Wt %)	11.8	9.5
9.4		

Source : Hardin , 1992

Table II-2-2 Typical properties of delayed petroleum coke

(Ultimate analysis as received , Weight %)

<u>Constituent</u>	<u>Average</u>	<u>Range</u>
Carbon	79.74	75.0 – 86.0
Hydrogen	3.31	3.0 – 3.6
Nitrogen	1.61	1.3 – 1.9
Sulfur	4.47	3.4 – 5.8
Ash	0.27	0.0 – 0.6

Oxygen	0.00	0.0 – 0.1
Moisture	10.60	5.5 – 15.0
HHV , MJ / Kg	31.3	29.3 – 33.7
Ash Properties ,ppm	<u>Average</u>	<u>Range</u>
Vanadium	> 2,000	500 – 2,000
Nickel	336	250 – 450
Iron	84	50 – 250
Volatile Matter , %	10	8 – 16

Source : World Bank Technical Paper Number 286 .

Table II-2-3 Advantages and disadvantages of petroleum coke :

Parameter	Advantages / Disadvantages
High heating value	* Results in lower handling cost per G.J *Blending improves combustion of subbituminous .
Low volatile Matter	*Has possible ignition problem * May require supplemental fuel
Low Ash Content	* Reduce Ash handling cost
High vanadium/ other metals	* May make fly ash more saleable . *Leads to deposits and corrosion problems.
High Sulfur Content	*Inhibits ability to meet SO ₂ emissions produces solid waste and may lead to high disposal cost. *Leads to acid dew point problems .
Low Grindability index .	* Reduce Pulverizing and maintenance cost .

Source : World Bank Technical Paper Number 286 .

II-2-11 Overview of delayed coking process :

There is a general thrust in the petrochemical industry to reduce waste and energy consumption . Delayed coking is a waste minimization process , used to convert petroleum residue into useful liquid and gas product streams . Thus , there is a great deal of emphasis with in the petroleum industry to reduce cost , improve safety in operation and maintenance of coking units . This can be realized through process improvement , optimization and reduction in replacement of high cost capital equipment .

Delayed coking is a thermal cracking process used in petroleum refineries to recover liquid and gas product streams from crude oil residue . The feed stream , which mainly consist of vacuum reduced crude (VRC) , is heated in a fired heater to about $485 - 505^{\circ}\text{C}$ so that it attains thermal cracking temperatures (Harbi 2001) . The residence time in the furnace is very short and coking is delayed until the feed reaches the large coking drums downstreams of the heater . This a batch – continuous process where the flow of feed stream is continuous . The feed stream is switched between two drums . One drum is on – line filling with coke while the other drum is being cooled , decoked and warmed up . The entire process consist of the

following steps : The empty drum is initially heated using hot vapor . During this process heat is transferred to the drum walls and the condensed vapor is continuously drained out of the drum from the bottom . After the cold drum has been vapor heated , hot oil from a tube furnace at about 485 °C is injected into the drum . Most of the hot vapor condenses on the colder walls of the drum , and a large amount of liquid runs down the sides of the drum into a boiling pool at the bottom of the drum . The liquid at the bottom of the drum starts to heat up to coking temperatures . The liquid pool slowly turns to solid coke . Steam – stripping is carried out before and immediately after the feed stream is switched to the second coke drum . Steam – stripping transfers heat from the bottom section of the coke bed to the unconverted liquid present at the top of the coke drum and also prevents plugging of the coke bed .

Plugging of the coke bed causes problems in cooling the coke since sections of the bed will be isolated from the steam and cooling water . Coke is then cooled by flowing water through the bed . The final stage involves cutting and removal of coke from the drum , (Ellis 1993) .

II-2-12 Process description :

In delayed coking , the feed material is typically the residuum from vacuum distillation towers and frequently includes other heavy oils . The feed is heated by a fired heater (furnace) as it is sent to one of the coke drums (Adams 1994) .

The feed arrives at the coke drum with a temperature ranging from 870 to 910°F .

Typically drum overhead pressure range from 15 to 35 psig . Under these conditions , cracking proceeds ,and lighter fractions produced are sent to a fractionation tower where they are separated into gas , gasoline , and higher value liquid products . A solid residum of coke is also produced and remains with in the drum .

After the coke has reached a predetermined level with in the on oil drum , the feed is diverted to the second coke drum . The use of multiple coke drums enables the refinery to operate the fired heater and fractionation tower continuously . Once the feed has been diverted , the original drum is isolated from the process , flow and is refered to as the off oil drum . Steam is introduced to strip out any remaining oil , and the drum is cooled (quenched) with water , drained , and opened (unheaded) in preparation for decoking . Decoking involves using high pressure water jets from a rotating cutter to fracture the coke bed and allow it to fall into the receiving area below . Once it is decoked , the off oil drum is closed (re – headed) , purged of air , leak tested , warmed – up , and placed on stand – by , ready to repeat the cycle . Drum switching frequency ranges from 10 to 24 hours .

33

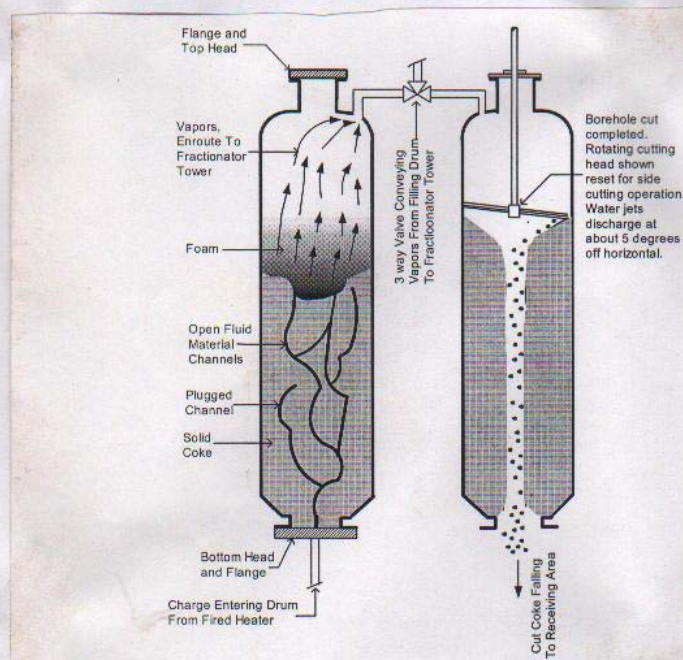


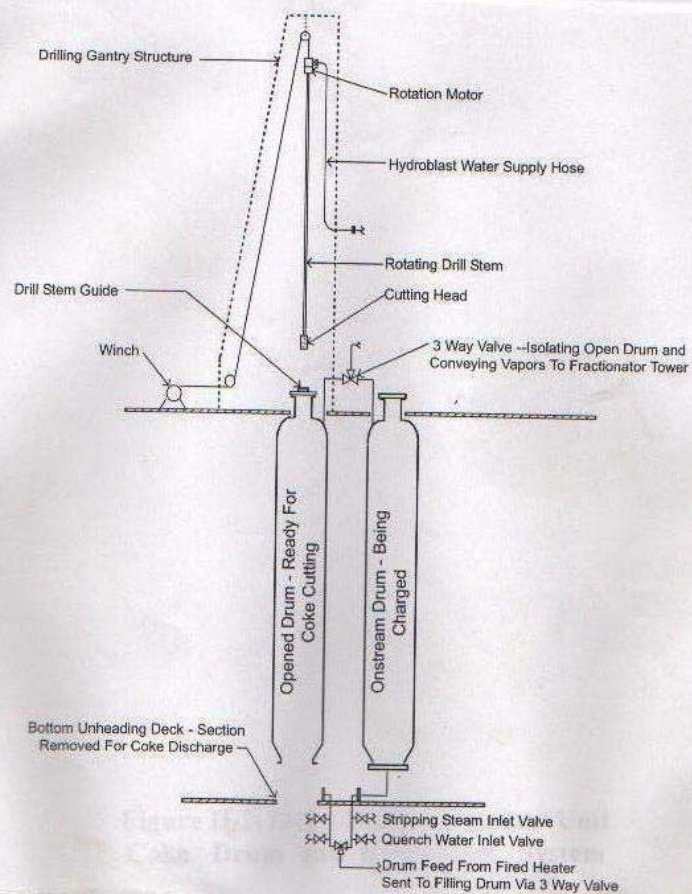
Figure II-2-12-1 Delayed coker Unit cutaway to Depict Drum in Filling and migration Mode (Left) and Drum in cutting Mode (Right)

Source : OSHA 2001 .

Figure II-2-12-1 Delayed coker Unit cutaway to Depict Drum in Filling and migration Mode (Left) and Drum in cutting Mode (Right)

Source : OSHA 2001 .

34



**Figure II-2-12-2 Delayed Coker Unit
Coke Drum and Hydroblast System**

Source : OSHA 2001 .

**Figure II-2-12-2 Delayed Coker Unit
Coke Drum and Hydroblast System**

Source : OSHA 2001 .

II-2-13 Specific operation hazards :

1- Coke drum switching :

Most delayed coker unit operations (DCU) consist of several DCU modules ,each typically alternating between tow coke drums in the coking /decoking sequence . Some DCU modules include a third drum in this sequence . Each drum includes a set of valving , and each module includes a separate set of valving . Differences in valving among drums and among modules may be difficult to distinguish and can lead to unintended drum inlet or outlet stream routing . Similarly , valve control strains , for remotely activated valves , may not always clearly identify the operating status of different drums and modules . Activating the wrong valve because of mistakes in identifying the operational status of different drums and modules has led to serious incidents .

2- Coke drum head removal :

Conditions with in the drum , during and after charging ,

Can be unpredictable.

Under abnormal conditions , workers can be exposed

to the release of hot water , steam and coke , toxic furnaces

and physical hazard during removal of the top and bottom

drum heads . The most frequent or severe hazards associated with this operation are described below :

i) Geysers / eruptions

Under abnormal situations , such as feed interruption or anomalous short – circuiting during steaming or quenching ,

hot spots can persist in the drum . Steam , followed by water , introduced to the coke drum in preparation for head

removal can follow established channels rather than permeate throughout the coke mass . Because coke is an excellent insulator , this can leave isolated hot areas with in

the coke . Although infrequent , if the coke with in the drum

is improperly drained and the coke bed shifts or partially collapses residual water can contact the isolated pockets of hot coke , resulting in a geyser of steam , hot water, coke particles , and hydrocarbon from either or both drum openings

after the heads have been removed .

ii) Hot tar ball ejection :

Feed interruption and steam or quenching water shorted – circuiting can also cause hot tar balls , a mass of hot (over 800 °c) tar – like material , to form in the drum . Under

certain circumstances , these tar balls can be rapidly ejected from the bottom head opening .

iii) Undrained water release :

Undrained hot water can be released during bottom head removal , creating a scalding hazard .

iv) Shot coke avalanche :

Sometimes , the coke forms into a multitude of individual various sized , spherical shaped chunks known as shot coke rather than a single mass . In this situation , the drum contents are flowable and may dump from the drum when the bottom head is removed creating an avalanche of shot coke .

v) Platform removal / falling hazard :

Some DCUs require the removal of platform sections to accommodate unheading the bottom of the drum .

This can introduce a falling hazard .

3- Coke cutting (hydroblasting operation) :

Coke – cutting or hydroblasting involves lowering from an overhead gantry a rotating cutter that uses high pressur (2000 to 5000 psig) water jets .

The cutter is first set to drill a bore hole through the coke bed . It is then reset to cut coke away from the drum interior walls . Workers around the gantry and top

head can be exposed to serious physical hazards , and serious incidents have occurred in connection with hydroblasting

operation . Some of the most frequent and sever hazards are described below :

- i- If the system is not shut off before the cutting nozzle is raised out of the top drum opening , a high pressure water jet can be exposed and seriously injure even dismember a nearby worker .
- i- Fugitive mists and vapors from the cutting and the quench water can contain contaminants that pose a health hazard .
- ii- The water hose can burst while under high pressure , resulting in whipping action that can seriously injure nearby workers .
- iii- The wire rope supporting the drill stem and water hose can fail (part) , and wire rope to fall onto work areas .
- iv- Gantry damage can occur , exposing workers to failing structural members and equipment .

4- Coke transfere , Processing and storage :

The following coke conveyance , processing , and storage operations have presented safety and health hazards for DCU workers :

- i- The repositioning of rail cars by small locomotives or cable tuggers to receive coke being cut from a drum can create physical hazards for workers in the rail car movement area .
- ii- Mechanical conveyors and coke crushers may contain exposed moving parts that can cause fracture or crush type injuries at pinch points .

Fires are common in coke piles and rail cars . Large chunks of coke can contain pockets of unquenched material at temperatures well above the ignition point. When fractured and exposed to air , this material can ignite . Fires have also been

attributed, although less frequently , to reactions that.

lead to spontaneous combustion .

iii - Combustion products and oxygen depletion resulting from spontaneous fires can create hazardous

conditions for workers in confined spaces .

iv - Wet coke in an enclosed area has been reported

to have absorbed oxygen from the surrounding air under certain circumstances . This can make the area

oxygen deficient and cause asphyxiation .

5- Emergency evacuation :

The delayed coking process is very labor intensive . Each batch process cycle requires 25 or more manual operations (valve , winch operation , drum heading , etc.) and many DCUs operate with three or more sets of drums . Tasks are performed at several levels on the coke drum structure . The upper working platform (frequently called the cutting deck) is generally well over 120 feet above ground . During an emergency , evacuation from the structure can be difficult .

In addition , moisture escaping from drum openings during cold weather can produce fog . This can obscure vision and make walkways , and hand rails wet and slippery , creating additional difficulties during emergency evacuation .

6-- Toxic exposures, dust irritants , and burn trauma:

DCU workers can be exposed to coke dust and toxic substances in gases and process water around DCU operations . Workers can also be exposed to physical stress and other hazardous conditions . The following exposures to toxic substances , irritants , and hazardous conditions have been associated with DCU operations , in general :

- i) Hot water , steam , and liquid hydrocarbon (black oil) can escape from a coke drum and cause serious burn trauma. Contact with black oil can cause second or third degree burns . In addition , liquid hydrocarbon escaped from a coke drum can be well above its ignition temperature , presenting a fire hazard .
- ii) Heat stress can be a health hazard during warm weather , particularly for those required to wear protective clothing while performing tasks on the coke drum structure .
- iii) Hazardous gases associated with coking operations , such as hydrogen sulfide , carbon monoxide , and trace amounts of polynuclear aromatics (PNAs), can be emitted from the coke through an opened drum or during processing operations .
- iv) If allowed to accumulate and become airborne , dust around a DCU may exceed acceptable exposure limits and become a hazard .

II-2-14 Controlling the hazards :

Evaluating hazardous conditions , modifying operations
to

Control hazards , actively maintaining an effective
emergency response program , and familiarizing workers

about risks and emergency procedures will help reduce the frequency and severity of serious incidents associated with DCU operations .

II-2-15 Specific operation hazards :

a. Coke drum switching :

No one system has proven effective in eliminating all incidents associated with incorrect valve activation due to mistaken coke drum or module

identification , however , the following actions have

been reported as beneficial :

- i) Conduct human factors analysis to identify , evaluate, and address potential operator actions that could compromise the safe operation of the coke drum system .
- ii) Provide interlocks for automated or remotely Activated valve switching system .
- iii) Provide interlocks for valves that are manually operated as part of the switching / decoking cycle to avoid unanticipated valve movement .

- iv) Color code and clearly label valves and control points to guard against incorrect identification .
- v) Provide indicator lights at valve and valve control stations to help the operator determine which is the correct valve station for the intended operator action .
- vi) Use the buddy system (employees working in pairs) to help verify accurate valve or switch identification .
- vii) Conduct periodic and documented training focusing on the importance of activating the correct valve or switch and the consequence of incorrect activation .

b. Coke drum head removal :

It can be difficult to anticipate the presence of either a hot spot or a hot tar ball in the coke drum prior to drum head removal . In light of this possibility and the potential for serious incidents , it is prudent to :

- i) Be alert to any operating abnormalities or variations during charging , steaming , or quenching that may forewarn a hot spot or tar ball .

Have a contingency plan to deal with such issues before proceeding with coke drum head removal and coke cutting .

- ii) Always assume the possibility of a hot – spot induced geyser or the release of hot tar balls or undrained hot water , and incorporate protective operational measures in drum unheading operation . Further control the hazards by establishing restricted areas , minimizing the number of workers in restricted areas , minimizing the time spent by essential workers in restricted areas , and maintaining readiness for a rapid evacuation .
- iii) Consider equipment upgrades to further control the hazards associated with geysers and release of hot tar balls and undrained hot water during drum head removal , such as installing protective shrouds and automating both top and bottom head removal operations to keep workers away from these unprotected areas .
- iv) Consider emergency steam / cooling water sources in the event of loss of primary steam / cooling water supply or because of drum inlet flow path obstruction .

- v) Provide temporary guardrails to prevent employees from falling while platform plating is removed for bottom head removal .
- vi) Consider installation of vapor ejectors to draw vapors away from the open top head area .

c- Coke cutting (hydroblasting operation) :

The following actions could help control hazards associated with coke cutting operations :

- i) Install an enclosed cutters shack for workers protection – preferably supplied with air from a remote source to maintain slight positive pressure .
- ii) Ensure that personnel who must be on the coke drum structure when a drum is open wear prescribed personal protective equipment .
- iii) Conduct training in recognition and prevention of worker heat stress .
- iv) Make sure the interlocks will work to shut off and prevent restart of the cutting head is

raised above a predetermined point with in the coke drum .

Consider installing redundant switches against extracting a cutting head that is under pressure .

- v- Verify the adequacy of the inspection and maintenance program for cutting water hoses , wire ropes , and hoists .
- vi- Establish a gantry structure inspection and maintenance program . Periodically verify that gantry structures have not been weakened due to corrosive conditions , such as mist existing from the top nozzle , that could lead to gantry collaps .
- vii- Install drill stem free fall arresters .

7- Coke transfeere , processing , and storage :

The following actions could help control hazards associated with coke conveyance , processing , and storage operations :

- i) Establish and enforce restricted areas (e.g., areas where heavy equipment movement and possible lash path of a wire rope from failed equipment may occur) to prevent personnel entry and ultimately , injury .
- ii) Establish and periodically verify the operability of an alarm system that activates immediately before and

during heavy equipment (rail car , bridge crane , or conveyor movement .

iii) Verify conformance with a safe entry permit system to ensure that appropriate measures are taken prior to and during entry into any enclosed area or vessel where coke may be present .

iv) Establish personnel protective measures to protect against inhalation or personnel contact with coke dust or potentially contaminated mists from water used for cutting , quench , or coke conveyance .

II-2-16 Emergency evacuation – preparations and procedures:

Despite best efforts to prevent incidents , DCU operators should anticipate the need for emergency evacuation and other response measures , operate in a manner that will minimize the severity of an incident , and prepare for and implement emergency procedures to protect workers safety .

The following specific actions are recommended :

i) Review and address weakness associated with the location and suitability of emergency escape routes . Protected stairways , preferably detached from the coke drum structure, are the most effective conventional means of emergency escape route (egress) from tall structure ,

such as those serving coke drum . Consider installing horizontal walkways to adjacent structures .

Some refineries are exploring escape chutes . Also , slip resistant walking surfaces will help prevent falling during an emergency evacuation .

ii) Establish or verify the operability of an evacuation signal

(scram Alarm) to expedite personnel clearing the structure in

the event of an emergency . Alarm signal a caution (triggering) stations should be deployed at work areas and along the escape routes .

iii) Install water sprays to protect work stations and emergency escape routes . Include activation stations at work stations and along the escape route .

iv) Provide heat shields to protect work stations and escape routes . Ensure that the shield will not interfere with evacuation and will not entrap fugitive vapors .

v) Conduct regular emergency exercises to test the plan as well as to ensure familiarity with emergency signals , evacuation routes , and procedures .

11-2-17 Toxic exposures, dust irritants , and burn trauma :

The following actions could help control exposures to toxic substances , irritants , physical stress , and hazardous conditions associated with DCU operations , in general :

- i- Configure coke drum inlets and outlets with doubleblock valve and steam seal isolation to reduce the likelihood of unanticipated leakage .
- ii- Establish burn trauma response procedures , including procedures for interacting with emergency medical service providers and the burn trauma center that would be used in the event of a burn incident .
- iii- Conduct burn trauma simulation exercises to ensure appropriate use of the emergency response procedures and the training level of relevant personnel .
- iv- Evaluate health exposure potential and establish appropriate protective measures based on an industrial hygiene survey plan that anticipates variations in the range of DCU feed stocks and operating conditions .
- v- Shovel , sweep , vacuum , and provide proper ventilation to keep exposures to dust around a DCU to within acceptable limits

II-3 Modern delayed coking process :

The delayed coker is the only main process in a modern petroleum refinery that is a batch – continuous process . The flow through the tube furnace is continuous . The feed stream is

switched between two drums . One drum is on – line filling with coke while the other drum is being steam – stripped , cooled , decoked , pressure checked , and warmed up . The overhead vapors from coke drums flow to a fractionator , usually called a combination tower . This fractionator tower has a reservoir in the bottom where the fresh feed is combined with condensed product vapors (recycle) to make up the feed to the coker heater .

II-4 Delayed coking drum cycle :

Since the feed stream is regularly switched between drums , a cycle of events will occur on a regular interval depending on the delayed coking unit feed rate , drum size , and throughput capacity. Most typical delayed cokers currently run drum cycle times of about 16 hours with one drum filling on – line while its counterpart is off – line for stripping , cooling , and decoking . Drum cycle event approximate time requirements for such a cycle are shown below in Table 11-4 . Shortening the cycle time is one method of increasing throughput on delayed coking units . One refinery regularly runs 12 hours drum cycles and has attempted 10 and 11 hours cycles , but cycles this short are extremely difficult due to minimum time requirements for each of the steps of the drum cycle.

Table II-4 Typical Short Cycle Coking Operations

<u>Drum Cycle</u>	<u>Hours</u>
Steam to fractionator	0.5

Steam to blow Down	0.5
Depressure, Water quench and Fill	4.5
Drain	2.0
Unhead Top and Bottom	0.5
Cutting Coke	3.0
Rehead / Steam Test / purge	1.0
Drum Warm – up (Vapor Heat)	4.0
Total Time	<u>16</u>

Source : Harden 1992

II-4-1 Drum warm – Up (Vapor Heat) :

To prepare the cold empty coke drum to be put back on – line to receive the hot feed , hot vapors from the on –line drum are circulated into the cold empty drum . The hot 415°C (780°F) vapors condense in the cold drum , heating the drum to a target temperature of the around 340°C(650°F) . While the drum is heating , the condensed vapors are continuously drained out of the drum .

II-4-2 On – Line filling :

After the cold drum has been vapors heated for a few hours , hot oil from the tube furnace at about 485°C (905°F) is switched into the drum . Most of the hot vapors condense on the colder walls of the drum , and a large amount of liquid runs down the sides of the drum into a boiling turbulent pool at the bottom of the drum . The drum walls are heated up by the condensing vapors , so less and less vapors are condensing and the liquid at

the bottom of the drum starts to heat up to coking temperatures . A main channel is formed similar to the trunk of a tree . As time goes on the liquid pool above the coke decreases and the liquid turns to a more viscous type tar . This tar keeps trying to run back down the main channel which can coke at the top causing the channel to branch , so the limbs of the tree in the drum appear (Ellis 1993) .

This progresses up through the coke drum . Sponge coke , which includes needle coke , is formed from this liquid which remains in a quiescent zones between the main branches or channels up through the coker . The liquid pools in the quiescent zones slowly turn to solid coke . Shot coke has a different type of coke structure indicating that it is produced while suspended in the phase in the drum .

On top of the liquid layer is foam or froth . Paraffinic type feedstocks with some sodium present foam readily compared to aromatic feedstocks which tend to have smaller foam heights . Higher temperatures greatly decrease the height of the foam . At high temperature , needle coke has very small or no foam present . After the coke drum is filled , the hot oil is switched to the new drum .

II-4-3 Steam – stripping / hot spots :

Steam must be flowing before the switch and immediately after the switch , otherwise , the yet unconverted liquid feed on top of the coke bed will run down the channels which will coke

or solidify and plug the channels . The plugging of the channels causes problems in cooling the coke since sections of the coke bed will be isolated from the steam and cooling water by the plugged channels. This is the cause for hot spots and steam eruptions when cutting the coke . Cold water from the cutting nozzle hits the exposed hot coke which results in a steam explosion . This particularly hazardous when the pilot hole is being cut , since the drum is filled with a large quantity of hot water . A steam explosion during pilot hole cutting can cause the hot water to erupt out of the drum and has caused fatalities in the past (Ellis 1993) .

Steam stripping also serves to transfer heat from the hot bottom section of the coke bed to the unconverted liquid present at the top of coke drum . Adequate steam stripping increases the amount of recovered gas oil yield while at the same time reduces the amount of volatile matter and pitch left in the top section of the coke drum . After the steam has been flowing up through the coke bed for about thirty minutes with the vapors going to the fractionator , the vapor line is vented to blowdown system . Steam is increased for a short time or in some cases water is immediately introduced at the bottom of the drum which instantly vapor temperature in the drum may increase slightly at first before cooling due to the increased flow of steam up through the coker .

II-4-4 Water cooling / drum bulging :

The rate of cooling water injection is critical . Increasing the flow of water too rapidly can cause harden the main channels up through the coker without cooling all of the coke radially across the coke bed . The coke has low porosity (the porosity comes from the thermal cracking which then allows the water to flow away from the main channels in the coke drum . Porosity of delayed coke has been measured experimentally in the past by measuring water flow through cores about the size of hockey pucks cut from large chunks of needle coke from different areas of a commercial coke drum .

Most of the coke cores were found to have no porosity except the coke right at the wall which had some porosity . This explains problems that have been found to occur with drums bulging during cooling down . If the rate of water is too high , the high pressure causes the water to flow up the outside of the coke bed cooling the wall of the coke drum . Coke has a higher coefficient of thermal expansion than does steel (154 for coke versus 120 for steel , $\text{cm} / \text{cm} / ^\circ\text{C} \times 10^{-7}$) . This was measured in the transverse direction from a chunk of needle coke . The coefficient of thermal expansion for raw sponge coke is probably even greater than that of the needle coke tested .

II-5- DELAYED COKING UNIT HARDWARE :

A basic coker operation flow diagram is shown below in figure II-5-1 to illustrate some of the delayed coking unit hardware.

II-5- DELAYED COKING UNIT HARDWARE :

A basic coker operation flow diagram is shown below in figure II-5-1 to illustrate some of the delayed coking unit hardware.

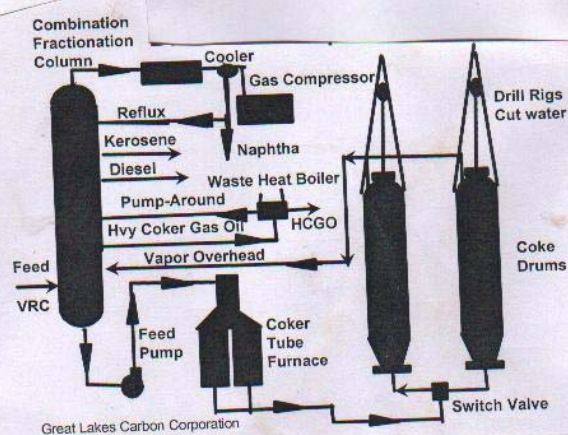


Figure II-5-1 BASIC COKER OPERATION

Source : Peter , 1983 .

Figure II-5-1 BASIC COKER OPERTION

Source : Peter , 1983 .

II-5-1 Feed preheater :

In some refineries , delayed coker feed which is usually vacuum reduced crude (VRC) arrives at the coker hot , straight from the vacuum distillation unit , but in most cases , delayed coker feed is relatively cold coming from tankage . The feed is preheated by heat exchangers with gas oil products or in some rare cases by a fired coker preheater (tube furnace) . In some refineries , the convection section of the main coker furnace is used to preheat the cold feed . The hot coker feed , ranging from 360 to 400°C (680 to 750° F) , then enters the bottom of the fractionator / combination tower where the fresh feed is

combined with some condensed product vapors (recycle) to make up the feed to the coker heater . The fractionator bottom provides some surge storage capacity for the incoming fresh feed , and in units , heat is transferred to the fresh feed by flowing a split of the fresh feed above the drum overhead vapor entrance to the fractionator . This practice usually results in increased amount of heavy coker gas oil recycle in the furnace charge .

II-5-2 Coker charge pumps :

The coker charge pumps located between the fractionator bottom and the coker heater are normally driven by an electric motor with a steam – driven turbine pump as a backup . The pressure is in excess of 35 bars (500 psig) with a mechanical seal operating up to 382°C (720°F) .

II-6 Coker tube furnace:

The coker tube furnace is the heart of the delayed coking process The heater furnishes all of the heat in the process . The outlet temperature of a coker furnace is typically around 500°C (930°F) with a pressure of 4 bars (60 psig) .

II-6-1 Coker furnace design:

Delayed coker furnace design objectives according to Elliott 1996 are :

- High in – tube velocities resulting in maximum inside heat transfer coefficient .

- Minimum residence time in the furnace , especially above the cracking temperature threshold .
- A constantly rising temperature gradient .
- Optimum flux rate with minimum practicable maldistribution based on peripheral tube surface .
- Symmetrical piping and coil arrangement within the furnace enclosure .
- Multiple steam injection points for each heater pass

Normally the modern – day furnace has two to four passes per furnace . The tubes are mounted horizontally on the side and held in place with alloy hangers . The furnace tubes are around 100 mm ID with 6 to 12 mm wall thickness and are at least a 9 % chrome alloy . Higher alloy tubes are being used with the more rapid steam spalling and steam – air decoking methods . Aluminized tubes have been tried , but offer no advantage . Multiple burners are along the bottom of the radiant wall opposite from the tubes and are fired vertically upward . The burners for each firebox are controlled by the temperatures of tubes in that firebox only . The control thermocouple for firebox should be three or more tubes back from the outlet to prevent coke forming on the thermocouple . The outlet thermocouple is initially read and an off – set from the control thermocouple is then used to control the furnace . Tall furnaces are advantageous since the roof tubes are less likely to have

flame impingement and overheating by both radiation and convection . Normally just the radiant section of the heater is used to heat the oil for a delayed coker . The upper convection section of the coker heater is used in some refineries to preheat the oil going to the fractionator or for other uses such as steam generator .

The typical gas burners in a delayed coker furnace are 3 MM BTU size . Adams(1994) stated that the burners will produce flame height of around 0.33 meter per 1 MM BTU . Elliott (1996) and others state that the average radiant flux rate should be below 9000 BTU/HR/FT² with cold oil velocity of 2 meters/sec (6 ft/sec) or mass velocity of 1800 Kg/sec/meter² (400 Ib/sec/ft²)or greater.

Velocity steam is added at around 1 wt % of the feed . This helps increase the velocity in the tube furnace , and reduces the partial pressure in the drum so that more gas oil product is carried out of the drum . The specific heat of the steam is less than the oil so steam is not a good source of heat in the drum . The main use for the steam is that it keeps the velocity flowing in the tube furnace if the oil flow is momentarily is lost or decreased which reduces the chance of coking up the furnace tube .

II-6-2 Heater tube decoking :

When coke forms in the heater tubes , it insulates the inside of the tube which results in elevated temperatures on the outside

of the tube . With good operational practices , coker furnace run length of 18 months are possible before decoking of the tubes is needed . When temperatures approach 677°C (1250°F) on the exterior skin thermocouple , the furnace must be steam spalled and/or steam – air decoked or cooled down and cleaned by hydraulic pigging .

II-6-3 Steam spalling:

Steam spalling was probably first practiced by Exxon but was perfected by Lloyd Langseth while operating the cokers at Arco in Houston , Texas in the 1970s . He was able to operate a coker furnace over four years without shutting down by practicing on – line steam spalling . The only reason he had to shut down was that Texas had a law that required steam boilers to be inspected every five years .

On – line steam spalling requires replacing the oil with steam in the pass and then heating and cooling the tubes to snap or spall off the coke inside tube . The steam and coke go into the drum . The main problem is in controlling the velocity and speed of spalling off the coke . Too rapid spalling can plug the tube outlet , and too high steam velocity can erode the metal in the elbows . In one refinery , return bends failed after the second steam spalling . Steam spalling requires that the delayed coker be supplied with four passes or more .

Attempts to steam spall a two – pass furnace has been tried , but the large amount of steam being handled caused problems in the fractionator .

II-6-4 Steam – air decoking and pigging :

The usual method of decoking the tubes in a coker furnace is to take the furnace off – line , steam spall , then burn the coke out of the tubes by steam – air decoking . After steam – air decoking , the tubes need to be water washed since the salts still remain in the tubes and will cause rapid coking of the tubes . A new method of decoking the tubes is to steam spall , and then use water pressure to push Styrofoam pigs with studs and grit on the exterior through the tubes and around u – bends (even u – bends with clean – out plugs). The pigs scrape out the coke without scratching the tube walls . Early methods of pigging coker heaters left scratches on the tube walls , but with the grit – coated pigs , pigging just polishes the inside of the tube wall . Pigging is faster than steam – air decoking , and refiners generally have longer campaigns on the heater compared to steam – air decoking .

II-6-5 Heater tube deposits :

Iron sulfide is probably not totally removed in steam – air decoking . Coke deposits have very high content of iron , silica , and sodium . Deposits recovered from bend clean – out plugs are sometimes long cylindrical shapes and in another case

looked like scallop shell . These deposits were mostly sodium and calcium .

II-7 Transfere line and switch valve :

II-7-1 Transfere line :

The line from the furnace to the switch valve and on to the drum is referred as the transfer line . The transfer line must be very well insulated to prevent coking and plugging . The shorter the line the better . Long transfer lines with many crosses and tee s used for clean outs will rapidly coke and increase the pressure on the furnace which usually results in increased fouling of the tubes in the furnace .

Flanges near the drums are difficult to insulate without causing the joints to leak . Some transfer lines have a pressure relief valve in the line , but most furnaces and transfer lines are designed to withstand the maximum pressure the charge pump can produce in case of an accidental switch into a blinded valve .

II-7-2 Switch valve :

The switch valve is a three – way valve with ports to the two drums and a port (recirculation line) back to the fractionator which is used in startup and shutdown . Older cokers used a manually operated Wilson – Snyder valve which was a tapered plug valve that required unseating before rotation . The newer units and retrofits are using ball valves which are usually motorized . One problem with the ball valves is that

many separate steam purge lines are required to keep coke from forming on the seal bellows . If the steam purges are not monitored they can decrease the temperature of the oil going to coke drum resulting in high volatile matter coke being produced .

II-8 Coke drums:

The coke drum diameters range from 4 to 9 meters (13 to 30 ft) with the straight side being around 25 meters (82 ft) with a 1.5 meter diameter top blind flange closure and a tow meter diameter bottom blind flange in which the 15 to 30 cm diameter inlet nozzle is attached . Both the top blind flange and the bottom must be removed when decoking the drum . Usually the drum is constructed from 25 mm of carbon steel and is clad internally with 2.8 mm of stainless steel for protection against sulfur corrosion . The pressure ranges from 1 to 5.9 bars , typically around 2 to 3 bars . The vapor outlet nozzles , 30 to 60 cm diameter , are located at the top of the drum . Pressure relief valves are also located on the top of the drum on modern cokers . The outside of the drum is insulated with around 10 cm (4 in.) of fiberglass insulation with an aluminum or stainless steel covering . The coke level in the drum is usually determined with three nuclear backscatter devices mounted on the outside of the drum .

II-9 Overhead vapor lines :

The vapor overhead line run from the top of the coke drum to the fractionator . The temperature in the line is around 443°C (830°F).

The temperature is decreased by about 28 °C (50°F) by injecting hot heavy coker gas oil into the line as quench oil . This prevents coking in the line . The heavy coker gas oil is a wash oil coating the inside of the pipe . If the liquid layer dries out , coke starts to form . Some refineries leave the insulation off the overhead lines to help drop the temperature and keep the inside wetted . Prevention of coke in the line is important since this will increase the pressure in the coke drum thus increasing reflux of gas oil in the drum . Decreasing coke drum pressure increases liquid yield (decreases coke yield) . Also, high pressure drops in overhead lines can cause foaming in the coke drum during the drum switch . Vapor line sizes are very large in order to obtain the minimum amount of pressure drop . One refinery used two 760 mm (30 inch) vapor lines in parallel .

II-10 Antifoam injection system :

Injection of silicon antifoam should always be furthest away from the vapor overhead line outlet at the top of the drum to prevent silicon from being carried overhead into the vapor lines to the fractionator . The heaviest possible antifoam that can be handled in the refinery should be used . Lower viscosity antifoams appear to break down at lower temperatures and are not as effective . Usually a carrier stream is used to carry the

antifoam into the drum, heavier carrier material would not be as easily flashed off in the drum . Several are using less antifoam and having less problems with since starting continuous injection of antifoam .

A Dow chemical company representative stated in 1981 that it is easier to prevent a foam than it is to kill a foam . Also , when a foam is broken down , it still a mist which can cause coking in the bottom of the fractionator . A rule of thumb is that antifoam should cost around \$0.10 per ton of coke produced . Costs different than this may indicate that too much or too little antifoam is being used .

II-11 Coker fractionator :

The fractionator or combination distillation tower separates the coker overheads into gases , gasoline , diesel , heavy coker gas oil (HCGO) , and recycle . An oversized fractionator can be used to maximize the amount of diesel product and minimize the heavy coker gas oil to the FCCU . Hot overhead vapors can cause coking in the lower section of the fractionator if trays are not kept washed (wet) . The major amount of heat is removed in the heavy coker gas oil section by trapping out the oil and then extracting the heat with heat exchangers or steam boilers . This pump – around HCGO is then pumped back into the tray above the trap – out tray . Some of the HCGO is sprayed below the trap – out tray to wash and cool the hot vapors . Trap – out trays can be used to catch some of this oil and reduce the

amount of recycle oil going back to the furnace . Packing can be used in fractionators to reduce the pressure drop , but it is critical to keep the packing wet to prevent coking in the packing . The pressure in the fractionator and also the coke drum is controlled by the gas compressor at the top of the fractionator .

The fresh feed from the vacuum distillation (VRC) should go directly to the bottom of the tower since the effective temperature of distillation is higher than in the fractionator . Originally when some cokers were designed to coke atmospheric reduced crude , the feed was sprayed into the fractionator above the vapor inlet to fractionate out more light ends in the feed . If VRC is injected above the vapor it condenses out part of the HCGO into the bottom of the fractionator increasing the recycle to the coker furnace . The bottom of the fractionator should be operated at as high a temperature as possible without causing coking in the bottom in order to keep the tube furnace duty low . Normally the temperature in the bottom ranges from 343°C (650°F) to 382°C (720°F) without coke formation in the bottom of the fractionator . A slotted stand pipe in the bottom of the fractionator feeds the furnace charge pump .

II-12 Hydraulic coke cutting system :

II-12-1 Cut water pump :

High pressure water is used to cut the coke out of the drum . Water pressures range from 86 bars (1250 psig) to 275

bars (4000 psig) and flow rates range from 2.8 cubic meters per minute (750 GPM) to 4.7 cubic meters per minute (1250 GPM) . Cut water pump are multistage barrel type or split case multistage pumps which were originally developed for feed water pumps for steam boilers . The pumps are usually powered with an electric motor , but some older units use steam – driven turbines .

II-12-2 Cutting equipment:

Derricks are built on top of the drum so that the drill stem (5 to 6 inch extra heavy pipe) can be moved with a winch and cable . The high pressure water flows through an API 10,000 psi drilling hose to the top of the drill stem . The drill stem is rotated with an air motor at the top through a rotary joint . The cutting nozzles are the pilot bit with down facing nozzles and the cutting bit with nozzles facing outward . New units have both nozzles incorporated into a single drilling head .

II-12-3 Coke cutting technique :

A pilot hole approximately one meter in diameter is drilled from the top of the drum to the bottom . The pilot hole must be cut down through the coke with minimum weight on the bit , since if pushed , the bit can follow the main channel in the coke drum , bend , and stick the drill stem in the coke . After completing the pilot hole , the pilot bit is changed to the cutting bit , and the bottom of the hole is belled out and opened up to around two meters in diameter to prevent plugging . The bit is

then pulled to the top of the drum and cutting begins by spiraling downward at four to six RPM with vertical movement of on – half meter per revolution of the drill stem . Usually a vertical four meter section will be cut by moving the drill stem up and down until the coke is all cut out of the section . Normally around 15 to 20 minutes are required to drill out the pilot hole and three to four hours to cut the coke . The coke can be cut directly into rail cars , cut into a crusher car and the coke pumped hydraulically , or cut into a pit or pad with cranes or end loaders moving the coke .

II-13 Review of FLUID COKING and FLEXICOKING technologies:

FLIUD COKING and its subsequent technology, FLEXICOKING are both well established processes with a total of 18 units constructed since the first commercial FLUID COKING unit stared up at the Exxon Mobile plant in Billings , Montana in 1954 . These technologies provide additional hydrocarbon conversion capability to the refinery for transforming the heavier fractions of the crude oil (650°F– plus boiling range) into the lower boiling range , higher value liquids (30°F to 950°F) . Both technologies are based on fluid solids reactor concepts .

FLUID COKING is a non – catalytic , carbon rejection process for converting heavy hydrocarbon feeds into lighter liquid products with investment levels on par with delayed

coking (at comparable feed rates) . Feedstock capabilities range from atmospheric residuum , vacuum residuum , deasphalter bottoms to oil sand bitumen ,with the advantage that some of the feed contaminants (i.e. , metals , Conradson carbon (CCR) , sulfur , nitrogen) are rejected to the produced coke , typical to thermal conversion . Some typical values for the rejection of these contaminants are summarized in the Table below .

Table II-13-1 Rejection of Contaminants by thermal conversion processing :

	Rejection	From	Liquids (% of feed)	
	<u>Sulfur</u>	<u>Nitrogen</u>	<u>Nickel</u>	<u>Vanadium</u>
Arab Heavy	32	97	95	95
Cold Lake Bitumen	34	79	99+	99+
Hondo	24	81	99+	99+

Source : D.G Hammond , 2003

FLEXICOKING is an extension of the FLUID COKING process that adds a third fluid solids vessel to the flowscheme to gasify up to 97 percent of the coke produced in the unit and includes low BTU gas desulfurization . While overall liquid yields are comparable , gasification of the coke produces a sweet , low BTU gas suitable for utilization within the plant or in neighboring facilities . Since the coke yield is converted to a clean fuel gas , FLEXICOKING technology maximizes the

overall plant yield of hydrocarbons through substitution of the low BTU gas for plant fuels .

Processes for the conversion of residuum are generally categorized into two types : carbon rejection or hydrogen addition . Hydrogen addition processes usually operate at high pressure (greater than 500 psi) and depend upon catalysis to achieve the desired reactions . Because of the use of a catalyst , deactivation by the heteroatoms and metals present in the residuum fraction generally occurs at significant rate operate at lower pressure (less than 60 psi) and utilize thermal cracking reactions to achieve the desired conversion of the high boiling molecules . Thermal cracking reactions refer to a number of types of reactions including cracking, condensation , polymerization and isomerization . This chemistry results in a redistribution of hydrogen in the feed hydrocarbons to yield liquid products with higher hydrogen – carbon ratios while the byproduct coke has decreased hydrogen – carbon .

II-14 Historical perspective :

The development of refining processes based on fluid solids technology began during the Second World War era with the commercialization of Fluid Catalytic Cracking (FCC) at the standard oil Baton Rouge refinery . After WWII and into the early 1950s , a large incentive existed for the development of a continuous process for converting residua , especially the heavy

vacuum tower residua , into more valuable products . Through the adaptation of fluid solids technology from catalytic cracking , FLUID COKING was developed extending the earlier thermal conversion technology . This development proceeded over the period , culminating in 1953 , and resulted in the construction and start – up of the first FLUID COKING unit in 1954 at the Carter Oil Billings Refinery . Over the next five years , seven additional units were started – up bringing the cumulative design capacity for FLUID COKING to nearly 120 kB/D . Of these eight units , three remain in operation today – the first Fluid Coker at the Billings Refinery (Exxon Mobile) and 2 other license units . Due to market conditions (demand for mogas and fuel oil) , no additional units were constructed until the late 1960 s when three additional FLUID COKERs were added were installed ,an additional 40 kBD of design capacity . During the same time frame , the late 1960 s , process development was initiated on FLEXICOKING . Environmental concerns in some regions indicated that the utilization of the high sulfur coke from FLUID COKING as a boiler fuel was going to be restricted . By gasifying the coke internal to the process would reduce this and other environmental concerns from the FLUID COKING process . The coke would therefore be converted into a clean burning fuel . During 1974 – 1975 , the FLEXICOKING process was demonstrated in a 750 B/D

prototype unit at the Esso Baytown Refinery . The unit operated for 16 months ,processing a wide range of residuum feedstocks (e.g., Boscan ,high metals ,Athabasca bitumen , high sulfur) . Start – up of the first commercial FLEXICOKING unit was in 1976 . Two years later , additional FLUID COKING capacity was started up . Between 1978 and 1986 , four additional FLEXICOKING units were constructed and started – up . Today , all five FLEXICOKING units remain in operation with seven FLUID COKING units operational . All total , these 12 units account for over 500 kBD of residuum processing capacity , approximately 12% of the total world – wide thermal conversion (delayed coking , FLUID COKING , and FLEXICOKING) capacity . Another single train of FLUID COKING at 95 kBD (vacuum residua basis) design capacity is under design and construction slated for start – up in 2004 .

II-15 Process description :

Both FLUID COKING and FLEXICOKING rely on thermal cracking process chemistries to achieve conversion of higher molecular weight hydrocarbon . The coke produced by that process chemistry is not only a product , but it also serves as a reaction media , a heat carrier and , in the case of FLEXICOKING, a reactant for steam/air gasification . These

technologies are therefore internally utilizing its lowest value product , coke .

II-15-1 FLUID COKING :

The principal process system consists of a fluid bed reactor and a fluid bed burner . In order to rapidly quench the product vapors from the thermal conversion reaction , a product scrubber is an integral component of the reactor , providing heat integration and initial fractionation . FLUID COKING can be operated in one of tow modes – conventional recycle versus once – through . In the recycle mode , all of the 975°F – plus material is converted to lighter products and coke . Typically , the feed , preheated to nominally 500°F, is introduced to the scrubber to be further pre – heated with the reactor overhead vapor stream . The scrubber pool achieves temperatures on the order of 700°F through this heat integration of colder feed with product gases from the reactor . The heaviest hydrocarbons in the product stream are there by condensed and co – mingle with the feed to be recycled to extinction in the reactor . While in the once –through mode , the 975°F– plus material is drawn off the scrubber and thus remains part of the heavy gas oil product . Another process variation is the vacuum pipestill integrated mode where by the cut point of rcycle steam is increased from

975°F to 1050°F . Figure II-15-1-1 provides a schematic diagram of the FLUID COKING process .

74

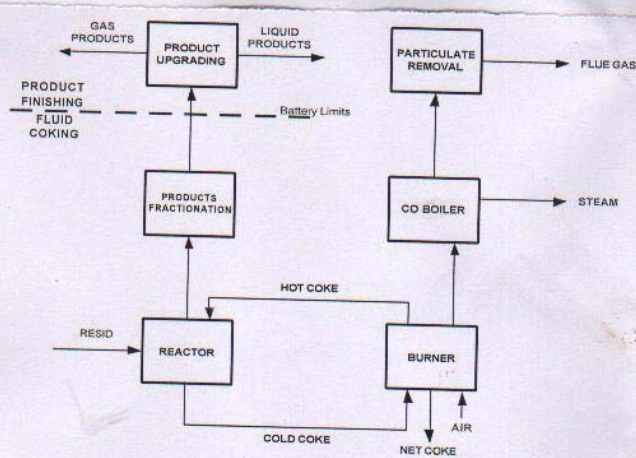


Figure II-15-1-1 FLUID COKING

Source : D.G Hammond , 2003

Figure II-15-1-1 FLUID COKING

Source : D.G Hammond , 2003

In the reactor , operating at temperature in the range of 950 – 1050°F , the heavy hydrocarbon feed (either fresh feed or the

fresh/feed recycle mixture) is injected onto the fluid bed of coke particles through a series of nozzles located on rings around the vessel . Several of these rings are oriented at different levels on the vessel . Through spraying onto the bed of the hot coke , the feed is thermally cracked into a full range of lighter products , from gases to gas oils , and by – product coke . The hydrocarbon vapors pass through the both the dense and the dilute phase of the fluid bed and into the reactor overhead system . The reactor overhead system consists of a set of cyclones for the recovery of coke particles , which are returned to the dense bed , and the reactor scrubber . Coke particle fines , which pass through the cyclones , are captured in the scrubber . Depending upon the mode of operation , these fines are either recycled to the reactor with the 975°F – plus stream or need an alternative removal scheme to protect downstream equipment . The hydrocarbon product flows from the scrubber to conventional fractionation , gas compression and light ends recovery facilities . The conventional fraction facilities used to separate the liquid products may incorporate its own light end facilities or may integrate with an other processing unit . Coke produced by the thermal cracking reactions is laid down on the bed coke particles , typically in a layering manner . In addition to the feed , steam , some mixed with the feed and some of it separate , is introduced to the reactor . This high temperature steam provides additional stripping of hydrocarbon vapors from

the coke particles to maximize the production of hydrocarbons . Steam introduced into the bottom of the reactor also serves to fluidize the coke particles . The overall coke inventory is maintained in the reactor by withdrawing the bed coke through the stripping section of the reactor , transferring over to the burner and by circulating hot coke back from the burner . Net coke is discharged from the burner . Heat required for the endothermic reactions of the process is supplied by circulating hot coke from the burner back to the reactor . Circulation of “cold coke” and “hot coke” is achieved using conventional standpipes , risers and slide valves . In FLUID COKING , particle size distribution of the bed coke is controlled using jet attritors located at the bottom of the reactor dense bed to reduce the size of the bed coke .

In the burner , a portion of the coke withdrawn from the reactor is burned using air (approximately 15 – 30 % coke consumption) , but the combustion is incomplete due to the fuel rich environment maintained in the burner vessel . Heat is therefore generated from the low value byproduct coke rather than the combustion of natural gas or fuel gas , more valuable streams . Burner operating temperature is in the range of 1100 – 1250°F. Nonetheless , the consumption of coke within the process eliminates the need for an external fuel supply . Heat and material balancing of the unit is achieved by removing the coke from the burner as a product stream . The feedstock metals

and heteroatoms (sulfur and nitrogen) are generally rejected to and are removed through the product coke stream . For further control of the particle size of the circulating coke , the larger particles are removed through a quench elutriator and the fines are returned to the burner vessel . The combustion of the coke produces a flue with a very low heating value that is typically feed to either a CO boiler or furnace to achieve further process heat integration . The heating value of this flue gas is approximately 20 Btu/scf with 40 % water , 55 % inerts . Pollution control equipment reduces the emissions of sulfur and particulates from the CO boiler .

II-15-2 FLEXICOKING :

Figure II-15-2-1 illustrates the process flow blocks FLEXICOKING is an extension of the FLUID COKING process to include the gasification of coke . Therefore , the reactor side elements of the process are the same as those for FLUID COKING, along with the cold coke and hot coke transfer lines . The nomenclature for the burner vessel is changed to heater vessel.

As illustrated in the figure a third vessel is added to the FLUID COKING process to gasify the coke with steam and air , producing synthesis gas (H_2 , CO , CO_2 , and inerts) . Operating temperature for gasifier is approximately 1700 – 1800 °F. The produced gas , along with entrained fines , is routed through the heater vessel for fluidization of the hot coke bed and

for heat transfer to the solids . Heat balancing for the reactor is achieved through the circulation of this heated coke and gasified coke . Gas leaves the heater through a set of cyclones and additional heat is removed through a steam generation train . Downstream of the heat recovery is a third stage of cyclones followed by a venturi scrubber to recover the remaining coke fines . The low Btu gas or synthesis gas is then treated for the removal of hydrogen sulfide . Typically , a small quantity of coke fines (approximately 3 %) is recovered in the heater overhead which purges metals from the heater /gasifier and additional coke can be withdrawn from the heater . Furthermore , partial gasification , which varies the yield of coke gas and therefore net coke , allows the flexibility to meet specific operating objectives .

79

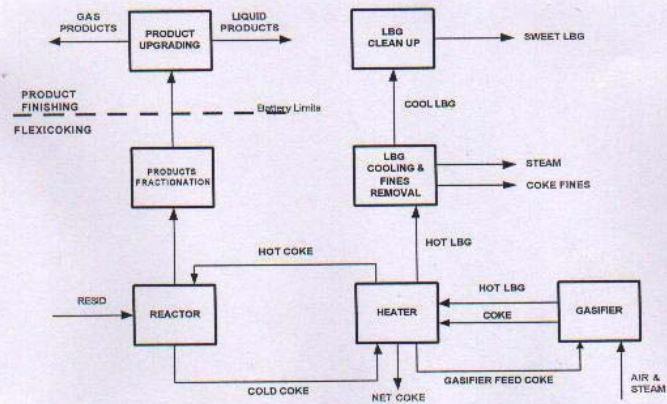


Figure II-15-2-1 FLEXICOKING

Source : D.G Hammond , 2003

Figure II-15-2-1 FLEXICOKING

Source : D.G Hammond , 2003

II-16 Products –yields, qualities and dispositions :

As with other thermal conversion processes , the products from FLUID COKING and FLEXICOKING are refinery intermediates and require further treating before leaving the refinery as final products . The liquid products boiling below 975°F have much lower levels of heteroatoms and metals than the feed residuum , indicating the significant rejection of these materials into the coke . The product liquids are also lower in density and boiling point than the feed residuum . Product yields and possible dispositions are illustrated in figure II-17-1 . A typical yield slates for processing vacuum residua (nominal output of 1050of) from Arab Heavy and Arab Light crudes are summarized in Table II-16 . A portion of the gross coke formed is burned for process heat requirements , therefore the product coke yield is only about 70 – 85 % of the gross coke . The yield of liquid products is comparable for both the FLUID COKING and FLEXICOKING processes .

Table II-16 Product Yields:

	<u>Arab</u>	<u>Resid</u>	<u>Arab</u>	<u>Resid</u>
--	-------------	--------------	-------------	--------------

	<u>LT.</u>		<u>Hvy</u>	
Component(wt%)	<u>Recycle</u>	<u>Once- Thru</u>	<u>Recycle</u>	<u>Once- Thru</u>
Product Gas (C4-minus)	11.2	9.8	12.9	11.2
Naphtha(C5-430°F)	15.3	13.3	14.4	12.5
Light Gas Oil (430 – 650°F)	12.1	10.7	10.2	8.9
Heavy Gas Oil (650 – 975°F)	34.7	30.0	27.1	24.1
Bottoms (975°F –plus)	0.0	12.3	0.0	12.2
Gross Coke	26.7	23.9	35.4	31.1

Source : D.G . Hammond , 2003 .

II-16-1 Reactor gas :

Yield of this stream is on the order of 10 – 13 wt % on fresh feed.

The C₄ – minus gas can be further separated and used within the refinery in a number of ways . The C₃/C₄ fraction can be separated and is usually treated further by caustic extraction / sweetening . The mixture can then be utilized as feed for alkylation , as LPG , as chemical feedstock , or polymerization in dimersol . C₄'s can be further separated , treated (caustic extraction / sweetening) and used in mogas

blending . The C_2 –minus component can be used as hydrogen plant feed or as refinery fuel gas after amine treating .

II-16-2 Coker naphtha :

Yield of this stream ranges from 12 – 15 wt % of fresh feed . Light coker naphtha is typically caustic treated and utilized as mogas blendstock . Heavy coker naphtha typically requires hydrotreating and then is utilized as either a reformer feedstock or as a mogas blendstock . Sulfur content for the naphtha is less than or equal to 1 wt % and the nitrogen is 0.01 wt % . Density ranges from 55 to 60° API . Coker naphtha can also be fed to FCC unit .

II-16-3 Coker gas oil :

Yield of this stream ranges from 24 – 27 wt % on fresh feed . The light coker gas oil stream can be hydrotreated and blended into the middle distillate pool or could be fed to a secondary conversion unit such as hydrocracking or FCC . Density of the light gas oil ranges from 25 – 29° API with sulfur between 2.8 to 3.6 wt % and nitrogen of approximately 0.1wt % . Severity for hydrotreating of this stream is dependent upon the product needs and the heteroatoms content of the feedstock . The heavy coker gas oil can likewise be fed to secondary conversion units or could be hydrotreated for blending into fuel oil stream . Usually , the heavy coker gas oil is hydrotreated prior to conversion in an FCC unit . Sulfur is in the range of 4.3 to 5.6 wt % and nitrogen , 0.4 to 0.6

wt% . This stream does contains conradson carbon (4 – 5 wt %) and metals (1 – 4 ppm) .

II-16-4 Bottoms :

The yield of the low value bottoms is approximately 12 wt % when the process is operated in the once –through mode . Conradson carbon of this stream ranges from 18 to 24 wt % and sulfur is of the range 4 – 6 wt % . The metals content (nickel and vanadium) is approximately 25 % of the feed content . The bottoms streams needs to be treated to remove solids , such as with hydroclones , but can be blended into fuel oil . Otherwise , this stream is recycled to extinction . One unit is currently operated in the once – through mode .

II-16-5 Product coke :

For either FLUID COKING or FLEXICOKING , yield of the gross coke ranges from 24 – 35 wt % on fresh feed basis . Coke yield is reduced for either of the crudes referenced when the once –through mode of operation is selected over recycle . The quantity of product coke is dependent upon the type of process . In FLUID COKING , only a portion of the coke is combusted . The coke is spherical in shape , 100 – 150 mm mean particle size , and is a non- agglomerating , free flowing solid . This fluid coke can then be sold into the solid fuels market with its product valuation based upon its chemical composition (sulfur and metals) and hardness characteristics . Potential outlets include cement kilns , where the cement adsorbs the sulfur –

containing combustion products from the coke , reducing the quantity of gypsum utilized , or boilers for steam and power generation . Fluid bed boilers for power production are an attractive outlet for fluid coke since this coke not require grinding or other preparation steps . According to SFA Pacific (petroleum coke markets – Pacific quarterly Report , 2002) fluid coke accounts approximately 5 % of the green petcoke produced world – wide in 2002 (3.4 M mt/yr of 79.5 M mt/yr) . A generic comparison of the green coke properties from Delayed coking and FLUID COKING is summarized in Table II-16-5-1 .

Table II-16-5-1 Green Coke property comparison :

	<u>Fluid Coke</u>	<u>Delayed Coke</u>
Moisture (as produced)	0.2 – 0.4	6 – 14
Volatile Matter (wt %)	4 – 7	8 – 14
Ash (wt %)	0.2 – 0.5	0.3 – 0.6
Bulk Density (lb/ft ³)	54 – 62	45 – 55
Gross Heating Value (Btu/lb)	12,000 – 15000	14,500 – 15000
Hardgrove Grindability Index	20 – 32	70 – 80

Source : SFA Pacific Quarterly Report , 1 Q 2000 .

In the case of FLEXICOKING , the yield of this stream is dramatically reduced (as low as 3 % of the gross coke) at maximum gasification of the gross coke . The purged coke

comes from the bed purge (at reduced gasification levels) , the tertiary cyclones or the venturi scrubber . Since this coke has been gasified , the sulfur content is less than 50 % of that in the gross coke . Disposition of the purged coke from FLEXICOKING can be into the solid fuels market , for metallurgical applications or to metals reclamation (nickel ,vanadium) .

II-16-6 Low BTU gas :

FLEXICOKING produces a low Btu gas , which is scrubbed with water to remove coke fines , and the content of H_2S in this gas is reduced to about 100 ppm though with FLEXSORB-SE or other amine scrubbing processes . The ratio of H_2 to CO is on the order of 1, but the gas contains approximately 50 mole % of nitrogen (on a dry basis) . Heat content (LHV) is in the range of 115 – 140 Btu/scf . This gas can be burned in a variety of commercially available burners (including pre-mixed ,and forced and natural draft) for use in process heaters and in utilities (steam generators , steam superheaters , gas turbine waste heat boilers) .

II-17 Material balance:

Estimating the process is operated in the once –through mode .

Drum cycle time = 16 hours .

Basis = fresh feed is estimated to be 1000 ton of Arab
Light vacuum reduced crude (VRC) per cycle .

Figure II-17-1 Product Dispositions from FLUID COKING

Source : D.G. Hammond , 2003 .

1- Reactor Gas :

Yield = 11 wt % .

Production = $0.11 \times 1000 = \underline{110}$ ton .

2- Coker Naphtha :

Yield = 15 – 20 wt % .

Average = 17.5 wt % .

Production = 0.175 x 1000 = 175 ton .

3- Light coker Gas Oil :

Yield = 12 – 14 wt % .

Average = 13 wt % .

Production = 0.13 x 1000 = 130 ton .

4- Heavy Coker Gas Oil :

Yield = 35 – 36 wt % .

Average = 35.5 wt % .

Production = 0.355 x 1000 = 355 ton .

5- Gross Coke :

Yield = 27 wt % .

Production = 0.27 x 1000 = 270 ton .

6- Net Coke :

Yield = 21 wt % .

Production = 0.21 x 1000 = 210 ton .

7- Flue Gas :

Yield on feed = 0.02 FOEB / Bbl Feed .

II-18 Process selection criteria:

Technology selection depends upon a number of criteria . Site – specific evaluations , balancing utilities and feed / product considerations , are required to determine the specific economics of an application of these technologies . FLUID COKING may be more attractive than delayed coking or other

thermal conversion processes for heavier residuum and/or for larger capacity trains . FLEXICOING may be more attractive in circumstances offering economically , attractive outlets for low BTU gas over production / sale of the coke or i0n cases where access to solid fuel markets is limited or restricted and there limited gas supplies . Relative to other thermal conversion technologies , FLUID COKING and FLEXICOKING offer a number of advantages :

- Continuous process .
- Feed and Operation Flexibility .
- Reliability .
- Train Capacity /Size .
- Environmental .

II-18-1 Continuous process:

Unlike delayed coking , FLUID COKING and FLEXICOKING are both continuous process in that feed is constantly on to the reactor . As such , the bath cycle aspects of delayed coking are avoided . These include process load swings on the fractionator due to drum cycling , frequent cycling loads on intermittent use equipment (e .g , coke drums) , and opening of equipment and potential exposure of personnel to process hazards . In delayed coking , reductions in cycle time are utilized as a means of increasing unit throughput . Such alterations in the process scheduling will further exacerbate the thermal cycling and subsequent stresses on process equipment .

Due to the continuous nature of the FLUID COKING and FLEXICOKING , these process have lower manpower requirements than delayed coking .

II-18-2 Feed and operations flexibility:

Both the FLUID COKING and the FLEXICOKING process can handle a wide assortment of feeds – atmospheric or vacuum residua , bitumen , deasphalter bottoms and other high boling hydrocarbons materials . All of the process configurations described earlier have been utilized for handling a variety of feedstocks available . The turndown capacity of these processes is approximately 60 % which provides the flexibility for responding to operations issues such as upsets , shutdowns , or other unusual operations within in the refinery . Furthermore , the continuous process avoid process load swings and thermal cycling experienced with delayed coking trains . A number of FLUID COKING and FLEXICOKING units have expanded with modest investment by increasing their coke withdrawal capacity .

II-18-3 Reliabilty:

The run lengths for FLUID COKING are typically 24 months between scheduled turnarounds . The longest run to date is 35 months . For FLEXICOKING , typical run lengths are of 30 months duration , with the longest being 39 months . These processes achieve high mechanical reliability (unit

service factors routinely exceed 90 percent) since they are not mechanically intensive processes . Some units are achieving service factors greater than 95 % . Figure II-18-3-1 summarizes the average run length for FLUID COKING and FLEXICOKING units over the course of the technologies's history . As evidenced by the data in the figure , both technologies have made considerable progress in improving their reliabilities up to the run lengths being achieved by units today . Routine maintenance , and therefore , the more labor intensive servicing , is planned and performed during the turnaround periods .

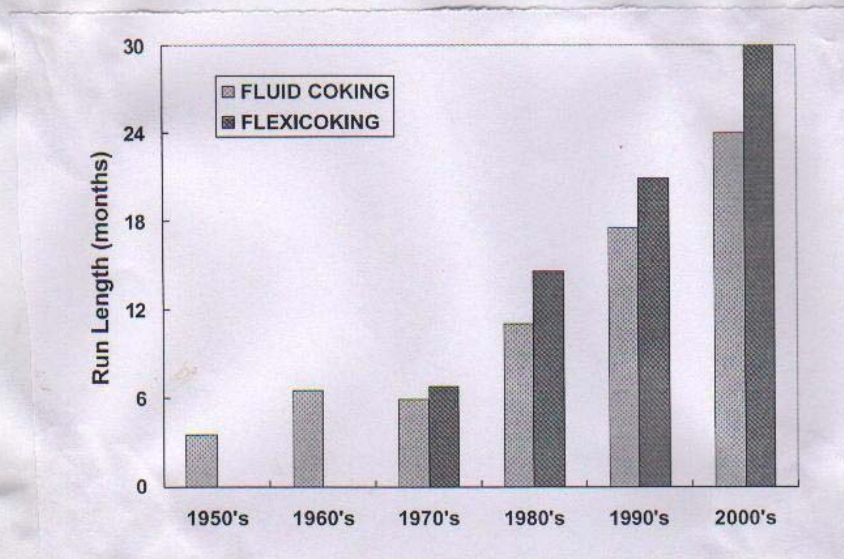


Figure II-18-3-1 Run Length History for FLUID COKING and FLEXICOKING

Source : D.G. Hammond 2003 .

**Figure II-18-3-1 Run Length History for FLUID COKING
and FLEXICOKING**

Source : D.G. Hammond 2003 .

II-18-4 Train capacity / size :

The fluid bed reactor systems offer large single train capacities , up to 95 kB /SD of vacuum residuum feed rate to a single vessel , with economy of scale minimizing overall investment levels and unit complexity . Large capacity increases have been achieved with relatively small capital investments .

II-18-5 Environmental:

Coke dust issues are minimized in FLUID COKING since the coke handling is an entirely closed system . With the process , coke circulation is through transfer lines and the transport of the product coke to the on – site and off – site storage silos is pneumatic . Flue gas from FLUID COKING is treated to handle potential pollution issues such as particulates and sulfur emissions . In addition to benefits described for FLUID COKING , FLEXICOKING offers some additional environmental benefits . Only 1 percent of the residuum feed to the unit is produced as net coke , while over 99 percent of metals in the feed are concentrated in this solid product . This not only controls the quantity of solid product shipped from the processing of a residuum feedstock , but also enables the potential economic recovery of metals from this stream . Also , 95 percent of sulfur in the residuum feed can be recovered as

elemental sulfur , generally within the battery limits of the plant

II-18-6 Economic comparison :

Comparison of relative economics for the upgrading of crude oil residues can encompass a number of process technologies depending upon the feedstock (atmospheric versus vacuum residua) and the technology type (carbon rejection versus hydrogen addition) . Both delayed coking and fluid coking , as carbon rejection technologies , offer conversion of residuum to clean process , especially in North America . Over the recent years several coking projects have been proposed and brought on – stream . A significant number of these projects are deicated to processing very heavy oils – either Venezuelan or Canadian . These process selection have resulted in continued interest in the economic comparison of these technologies , both within ExxonMobile and through independent consultants .

Historically , economic comparisons have illustrated that FLUID COKING was competitive or even more attractive than delayed coking . SFA pacific has recently completed an updte of its private , multi – client sponsored study⁵ comparing several processes for the upgrading of heavy crude oils to transportation fuels .

In general terms , the capital costs for FLUID COKING are lower than delayed coking , nominally by 15 – 20 % . On the other hand , the product realization for FLUID COKING is

lower . Therefore the results of an economic comparison are sensitive to the product yield and qualities of the technologies and the perspective product values placed on these streams . The SFA pacific study compares the net realizations calculated for four vacuum residues contrasting FLUID COKING to delayed coking . Based on the study , FLUID COKING provides net realizations equivalent to or better than that for the delayed coking case . Furthermore , the differential between the net realizations increases with heavier crude oils . In terms of the other dimentions of the economic analysis , FLUID COKING has inherent advantages such as its ability to handle heavier , more challenging crudes (elimination of furnace fouling concern) and its larger , single train capacity . In terms of heavier , more challenging crudes , FLUID COKING and FLEXICOKING can handle these feeds without dilution with a low boiling point solvent , a technique being used today to reduce furnace fouling tendencies in delayed cokers . In the case of FLEXICOKING , the solid by – product is further converted to low BTU gas . That conversion requires additional capital , approximately two – third more capital when compared to FLUID COKING .

II-19 Scanning Electron Microscope Examination (SEM) :

Different samples of petroleum coke from Elsiwez Refinery (Egypt) were examined before and after thermal treatment by means of SEM in order to investigate the presence of sulfur in the coke . (Ibrahim 1991) .

SEM showed that sulfur is distributed on matrix of untreated coke sample (Figure II-19-1) (Ibrahim 1991) .

The effect of thermal treatment on sulfur removal is seen in Figure (II-19-2) . From the figure it is obvious that few sulfur particles are present in the matrix of coke (Ibrahim 1991)

Figure II-19-3 showed some particles of sulfur on matrix of petroleum coke (Ibrahim 1991) .

The results given by Ibrahim (1991) have shown that after firing the samples of petcoke , the increase of temperature increase the percentage of sulfur removal and the low particle size enhances the percentage removal of sulfur .



Figure II-19-1 SEM Photo showing a distribution of sulfur particles on the matrix of petroleum coke (before treatment) (X = 6300)

Source : Ibrahim 1991 .

**Figure II-19-1 SEM photo showing a distribution of sulfur
particles on the matrix of petroleum coke
(before treatment)
(X = 6300)**

Source : Ibrahim 1991 .

97

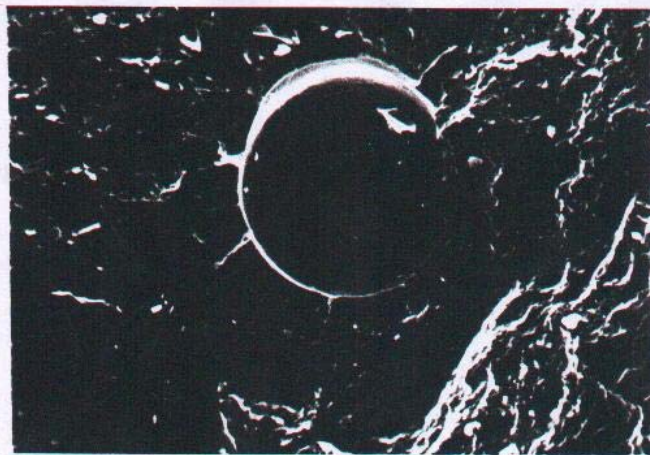


Figure II-19-2 SEM Photo showing a petroleum coke particles
of sample treated at 1000 °C
(X = 3500)

Source : Ibrahim 1991 .

**Figure II-19-2 SEM photo showing a petroleum coke
paricles of samples treate at 1000 °C
(X = 3500)**

Source : Ibrahim 1991 .



Figur II-19-3 SEM Photo showing some particles of sulfur on matrix of petroleum coke .
(X = 3150)

Source : Ibrahim 1991 .

**Figur II-19-3 SEM photo showing some particles of
sulfur on matrix of petroleum coke
(X = 3150)**

Source : Ibrahim 1991

II-20 Kiln system chemistry:

The chemical reactions occur in the kiln , the temperature is increased when going from the meal feed to the rotary kiln . The most important oxides that participate in the reactions are Ca CO_3 , SiO_2 , Al_2O_3 and Fe_2O_3 . Up to about 700°C water is removed from the meal . In the preheating section ($700 - 900^\circ\text{C}$) calcinations as well as an initial combination of alumina , ferric oxide and silica with lime takes place . Between 900°C and 1200°C bellite , C_2S ($= 2 \text{ CaO SiO}_2$) , forms .

Above 1250°C a liquid phase appears and this promotes the reaction between bellite and free lime to form allite , C_3S ($= \text{CaO SiO}_2$) . During the cooling stage the molten phase forms C_3A , tri calcium aluminate , ($= 3 \text{ CaO Al}_2\text{O}_3$) and if the cooling is slow allite may dissolve back into the liquid phase and appear as secondary bellite .

Usually the production of clinker is done so that one type of clinker allows the plant to manufacture several well – defined

types of cement that comply with the physical demands as specified by cement standards . (Alsop 1998) .

Figure II-20-1 shows the circulation of sulfur inside the rotary kiln

of cement when utilizing petcoke as a fuel .

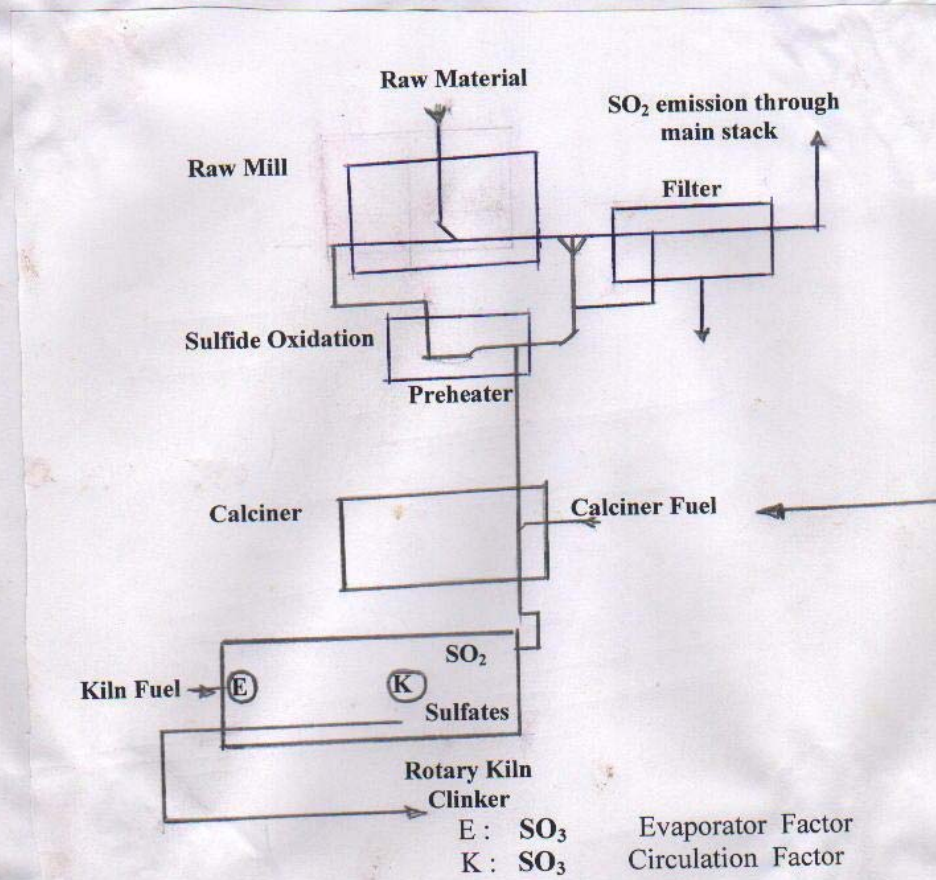


Figure II-20-1 Schematic illustration Of Sulfur Circulation

Source : Alsop , 1998 .

Figure II-20-1 Schematic illustration Of Sulfur Circulation

Source : Alsop , 1998 .

II-21 Process energy requirements :

The dominant use of energy in cement manufacture is fuel for the kiln . On average , energy costs in the form of fuel and electricity represent about 50 % of the total production cost .

The theoretical energy requirement for the burning process is about 400 – 430 Kcal/ Kg clinker . The actual fuel energy requirements , for different types of production process and kilns , are given in Table II-27-1. (Zevenhoven , 2000) .

Table II-21-1 Fuel Energy Requirements of Cement Kiln

System :

Process Type	Kiln Type	Fuel Energy Requirement (Kcal/Kg clinker)
Dry process	Kilns with cyclone preheater & precalciner	Literature 720
Dry process	Rotary Kilns with cyclone preheater	740 – 1000
Dry process	Long rotary Kilns	Up to 1200

Wet process	Long rotary Kilns	1200 – 1300
-------------	-------------------	-------------

Source : NEQS – Pakistan 2003.

In Atbara Cement Factory, fuel energy requirement is in the range of 1020 – 1040 Kcal / Kg clinker (Hamza 2005) .

The main users of electricity are the mills (finish grinding and raw grinding) and the exhaust fans (kiln / raw mill and cement mill) which together account for more than 80 % of electrical energy usage . The electricity demand is about 90 – 130 Kwh / ton of cement . (NEQS – 2003) .

In Atbara Cement Factory the electricity consumption in using fuel oil is 130 Kwh / ton of cement . (Hamza 2004) .

II-22 Fuel oil to coke switch over :

II-22-1 Facilities and equipment requirement:

Switching from fuel oil to petcoke , for combustion in cement kilns system , requires substantial capital investments , for additional facilities and equipment and changes in some existing

one .

Following is the summary of main facilities and equipments , required for such switch over :

- a – Raw petcoke storage facilities (open paved yards or sheds) .
- b – Petcoke mixing & crushing plant with loaders .

- c – Crushed petcoke piling facilities .
- d – Conveyor belt system , equipped with magnetic detectors and iron removal mechanism , to carry crushed petcoke to storage bunkers .
- e – Petcoke drying & pulverization mills , equipped with explosion prevention system .
- f – Pulverized petcoke feeders , equipped with pneumatic petcoke feed system .
- g – Petcoke burners (single – fuel or dual fuel) .

II-22-2 Operational consequence of switch over :

Introduction of solid fuel like petcoke in place of gaseous or liquid fuels in cement kilns , results into a more complicated fuel preparation as well as combustion system , which leads to the following operational consequences :

- a- Enhancement in professional attention and operational attendance on account of :
 - i - Initial experimentations and adjustments in the process and kiln operations during the switch – over stage .
 - ii - Continual increased process control and adjustments requirements due to increased batch – to batch variation in the fuel characteristics , associated with petcoke .
 - iii – Management of petcoke storage facilities including associated hazards of potential spontaneous petcoke fires .

iv – Management of additional petcoke handling , crushing , pulverization and feed operations associated hazards of potential petcoke dust fires and explosions .

b – Increase in labor requirements for petcoke handling , in – house transport and processing operations .

c – Increase in physical maintenance requirements on account of additional of facilities including petcoke loaders , petcoke crushers , petcoke pulverization mills , conveyor belts , storage bunkers , pulverized petcoke feeders and petcoke burners .

II-23 Air pollution : sources , impact and standard :

Air pollution is the main environmental issue with possible significant differential impacts , consequent to switching over from fuel oil to petcoke for cement production . Other issues of concern are potential hazards of spontaneous petcoke fires and petcoke dust explosion , potential contamination of soil and ground water from petcoke storage facilities and noise from petcoke processing facilities .

II-24- Emission sources:

The common sources and operations of air pollutant emissions , related to cement production irrespective of the type of fuel used , are as follows :

a – Raw materials crushers .

b – Raw materials mill .

c – Kiln system .

d – Clinker cooler .

e – Gypsum crusher .

f – Cement mill .

g – Fugitive emissions from raw materials quarrying and mining operations .

h – Fugitive emissions from transport of raw materials and finished product .

i – Fugitive from raw materials storage and handling facilities .

Following are the sources and operations , which can result into differential emission of pollutants , consequent to switch over from fuel oil to petcoke for cement production .

a- Kiln system .

b- Petcoke pulverization mill .

c- Fugitive emissions from petcoke storage and handling facilities .

II-25 Environmental impacts of principal air pollutants:

Following are the principal air pollutants released from operations and processes related with cement production :

a- Particulate Matter .

b- Oxides of Sulfur (SO_x) .

c- Oxides of Nitrogen (NO_x) .

d- Carbon monoxide (CO) .

Table II-31-1 Presents a summary of the potential impacts of the above air pollutants on environment and human life and health .

Table II-25-1 Impacts of Air pollutants on Environment and Human Health & Life :

Particulate Matter	E	Damage to plants , by choking the leaf pores and restricting photosynthesis .
		Global cooling of earth by reflecting back the solar radiation .
		Impairment of atmospheric visibility effecting transportation safety .
		Deterioration of aesthetic quality of atmosphere , land and water .
		Soiling of materials , physical properties and infrastructure .
	HL	Increase in the frequency of respiratory infections such as bronchitis .
Oxides of Sulfur	E	Chlorosis and plasmolysis in plant .
		Damage to materials and property , by acids rains , resulting from oxidation of sulfur dioxide to tri – oxide to sulfuric acid , after reacting with water vapor .
	HL	Serious lung damage , particularly in sulfate form .
		Respiratory diseases like chronic bronchitis .
Oxides of Nitrogen	E	Formation of photochemical oxidants .
		Damage to materials and property , by acid rains , resulting from oxidation of oxides of nitrogen to nitric acid , after reacting with water vapors .
		Retardation of growth in plants .
	HL	Reduction in oxygen carrying capacity of blood . Impairment of

		olfactory sense and night vision . Dryness and roughness of the throat .
Carbon Monoxide	HL	Heart attack , by reducing the oxygen carrying capacity of blood .
		Dizziness , head ache and nausea .
		Increase in reaction time of the drivers , a threat to the road safety .

E : Impacts on Environment .

HL : Impacts on Human Life and health .

Source : NEQS – Pakistan 2003 .

II-26 Emission standards :

Table II-32-1 Presents ranges of standard applicable to the cement production plant in different European countries .

For reference World Bank , Guidelines . (in mg /Nm³) .

Parameter	World Bank Emission	European countries Standard
Particulate Matter (> 10 micron) , Cement Klins Grinding , crushing , clinker coolers and related processes	50	50 – 150 50 – 400
Oxides of Nitrogen (NO _x)	600	500 – 1800
Carbon Monoxide (CO _x)	–	0.5

II-27 Stack emission from kiln system :

- **Main Pollutants :**

The main release from the kiln system during conversion of raw meal to clinker derive from the physical and chemical reactions involving the raw materials and the fuels . The main pollutants in the exit gases from a cement kiln system are as follows :

- a – Particulate Matter (PM) .
- b – Oxides of Sulfur (SO_x) .
- c – Oxides of Nitrogen (NO_x) .
- d – Carbon monoxide (CO) .

Other pollutants , which are generally not in high concentration , to be considered in relation to the production of cement are :

- a – Volatile Organic Compounds (VOC) .
- b – Polychlorinated Dibenzodioxin (PCDD) , and polychlorinated Dibenzofuran (PCDF) .

In all kilns systems , the solid material moves counter currently to the hot combustion gases . This counter current flow affects the release of pollutants . Many constituents , resulting from the combustion of the fuel or from the transformation of the raw material into clinker , are absorbed by or condensed on the raw material , during the course of their counter – current flow through kiln . The adsorptive capacity of the material varies with its physical and chemical state . This in tern depends on its position within the kiln system . For instance , material leaving the calcination stage of a kiln

process has high calcium oxide contents and therefore has a high absorptive capacity for acid species like HCL , HF and SO₂ .

II-28 Kiln emission flows :

Typical kiln exhaust gas volumes expressed as Nm³ per ton of clinker (dry gas , 101.3 KPa ,273 K) are between 1700 and

2500 for all types of kilns . (CEMBUREAU , 1997) .

Suspension preheater and precalciner kiln systems normally have exhaust gas volumes around 2000 Nm³ per ton of clinker.

II-29 Particulate Matter :

Traditionally the emission of particulate matter , particularly from kiln stacks , have been the main environmental concern in relation to cement manufacture . Other major sources of particulate matter are raw materials crusher , raw mills , clinker cooler , gypsum crusher , cement mill and coke pulverization mills .

Table II-29-1 presents particulate matter emission factors in Kg per ton clinker and emission concentrations in mg /Nm³ (dry gas , 101.3 Kpa and 0 °C) , for different types of process kilns and pollution control .

Type of kiln	Type of control	Emission factors Kg/ton	Emission concentrations mg/Nm ³
PH Kiln and	None	130.00	65,000

PH/ PC Kilns	ESP/ FF	0.10 – 0.20	50 – 100
Long Dry Kilns	ESP /FF	0.10 – 0.50	50 – 250
Wet Kilns	None	65.00	32,500
	ESP /FF	0.23 – 0.38	115 – 190

ESP Electrostatic Precipitator
FF Fabric Filter

Source : NEQS – Pakistan – 2003

One of the serious impacts of the use of solid fuels including coals for kiln operation is the potential increase in frequencies of short – term excessive carbon monoxide (CO) releases consequent to unsteady state operation of the combustion system , resulting from surges of solid fuel feeding , owing to poor fuel feeding controls . Control of CO levels is critical in cement kilns when electrostatic precipitators (ESP) are used for particulate abatement to ensure that the concentration are kept well below the lower explosive limit (typically to 0.5 % by volume) . If the level of CO in the ESP rises above this limit , then the electrical system is automatically switched off to eliminate the risk of explosion . (NEQS) .

II-30 Oxides of sulfur (SO_x) :

SO₂ is the main (99 %) sulfur compound released from the cement kilns , although some SO₃ is produced and , under reducing conditions , HS can be generated . SO_x emissions from cement kilns primarily depend upon the content of the volatile

sulfur in the raw materials , fuel sulfur , kiln type and extent of kiln gases diverted to the raw mill for drying purposes .

The SO_2 emission concentrations increase with increased levels of volatiles sulfur in the used raw materials and fuels . The volatile sulfur compounds are readily oxidized under high temperature conditions and presence of oxygen .

In pre – heater kilns , fuel and raw material sulfur , leads to much lower SO_2 emissions , due to the strong alkaline nature in the sintering zone , the calcination zone and in the lower stage of the preheater . The sulfur is mostly captured in the clinker . In contrast in long dry as well as wet kilns , the contact between SO_2 and alkaline material is not so good , and sulfur in the fuels can lead to significant SO_2 emissions . This fact is demonstrated in Table II-30-1 where reported values of emission factors for long kiln are much higher than for kiln equipped with preheaters .

Table II-30 1 presents uncontrolled SO_x emission factors in Kg per ton of clinker and emission concentrations in mg /m³

(dry gas , 101.3 k pa and 0 °C) , for different types of processes/ kilns .

--	--	--	--

Process / kiln Type	Type of control	Literature Emission factor (kg/ton)	Values Concentration (mg/ Nm ³)
PH Kilns and PH / PC kilns	None	0.27 – 0.50	135 – 250
Long dry kilns	None	4.9	2450
	DS	< 0.80	< 400
	AC	< 0.10	< 50
Wet Kilns	None	2.6 – 4.9	1300 – 2450

DS Dry Scrubber .
AC Activated Carbon .

Source : NEQS – Pakistan 2003 .

II-31 Oxides of nitrogen (NO_x) :

NO (nitric oxide) and NO₂ (Nitrogen dioxide) are the dominant oxides of nitrogen , in cement kiln exhaust gases , with no being more than 90 % . There are two main processes for production of NO_x as follows :

a -Thermal NO_x :

Thermal NO_x forms at a temperature above 1200 °C and involves the reaction of nitrogen and oxygen molecules in the combustion air .

b – Fuel NO_x :

Fuel NO_x is generated by the combustion of the nitrogen present in the fuel . Nitrogen in the fuel either combines with other nitrogen atoms to form N_2 gas or react with oxygen to form fuel NO_x .

Thermal NO_x is produced mainly in the kiln burning zone where it is hot enough to achieve this reaction . The amount of thermal NO_x produced in the burning zone is related to both burning zone temperature and oxygen content (air excess factor) . The rate of reaction for thermal NO_x increases with temperature , therefore , hard – to – burn mixes which require hotter burning zones will tend to generate more thermal NO_x than kilns with easier – burning mixes .

In a precalciner the prevailing temperature is in the range of $850 - 950^\circ\text{C}$, which is not high enough to form significant thermal NO_x , but fuel NO_x will occur . Therefore , in precalciner kilns where up to 60 % of the fuel can be burnt in the calciner , fuel NO_x formation significantly contributes to the total NO_x emission . The thermal NO_x formation in the these kilns is much lower when compared to long kilns where all the fuel is burnt in the sintering zone . Similarly , other types of secondary firing of fuel in the back end of a kiln system , such as in the kiln riser pipe of a suspension preheater kiln may give rise to fuel NO_x .

The above fact is reflected in Table II-37-1 where reported values of NO_x emission factors successively decrease from wet to long dry to preheater to precalciner / preheater kilns .

Besides temperature and oxygen content (air excess factor) , NO_x formation can be influenced by flame shape and temperature , combustion chamber geometry , the reactivity and nitrogen content of the fuel , the presence of moisture , the available reaction time and burner design .

Table II-31-1 Presents uncontrolled NO_x emission factors in Kg per ton of clinker and emission concentrations in mg/Nm^3 (dry gas , 101.3 K Pa and 0 °C) , for different types of processes / kilns

Process/ Kiln Type	Type of control	Literature Values	
		Emission Factor (Kg/ton)	Concentration (mg/Nm^3)
PH/PC Kilns	None	0.4 – 2.0 – 3.5	200 – 1000 1750
	SNCR	1.4 – 1.6	200 - 800
PH/ Kilns	None	1.3 – 2.9 – 5.9	650 – 1450 – 2950
Long dry Kilns	None	3.1 – 4.3 – 5.3	1550 – 2150 – 2650
Wet Kilns	None	1.8 – 4.9 – 9.8	900 – 2450 – 4900

SNCR Selective None – Catalytic reduction .

Source : NEQS – Pakistan 2003 .

II-32 Carbon monoxide (CO) :

The emission of CO is related to the content of organic matter in the raw material , but may also result from poor combustion , when control of the fuel feed is sub – optimal . Generally natural raw materials bring 1.5 – 6.0 gram of organic carbon per Kg of clinker into the process (Alsop 1998) . Tests have shown that between 85 – 95 % of the organic compounds in the raw material are converted to CO₂ in the presence of 3 % oxygen while at the same time remaining 5 – 15 % is converted to CO .

Table II-32-1 Presents uncontrolled CO emission factors in Kg per ton of clinker and emission concentrations in 0

(dry gas 101.3 K Pa and 0 °C) , for different types of processes kilns .

Process / Kiln Types	Type of control	Literature Values	
		Emission factor kg/ton	Concentrations (mg / Nm ³)
PH and PC Kilns	None	1.70 – 1.80	850 – 900
PH Kilns	None	0.50 – 0.80	250 – 400
Long dry kilns	None	0.11	55
Wet Kilns	None	0.40 – 0.8	200 – 400

Source : NEQS - Pakistan 2003 .

II-33 Volatile Organic:

In combustion process , in general , the occurrence of volatile organic compounds (and carbon monoxide) is often associated with incomplete combustion . In cement kilns , the emission will be low under normal steady – state conditions ,

due to the large residence time of the gases in the kiln , the high temperature and the excess oxygen conditions .

Concentrations may increase during start – up or upset conditions . These events can occur with varying frequency .

II-34 Emission of Volatile Organic compounds:

(VOC) can occur in the primary steps of the process (preheater , precalciner) , when organic matter that is present in the raw materials is volatilized as the feed is heated . The organic matter is released between temperatures of 400 and 600 °C . The VOC content of the exhaust gases from cement kilns typically lies between 10 and 100 mg/Nm³ . (NEQS) .

II-35 Stack emission from coke pulverization mill :

Coke pulverization mill is an important component of a coke based cement plant . Generally , hot flue gases from the kiln are introduced into the pulverization plant to dry the coke . The flue gas thus introduced , after carrying additional pollution loads from coke processing , leaves from the pulverization mill stack . The air flow used to dry the coke can not be reintroduced into the kiln due to the relatively high moisture and sulfur contents .

It implies that in case of coke as kiln fuel , the emissions originating from kiln are divided into two parallel streams , one emitting from the kiln stack and the other from the coke pulverization mill stack . A differential impact of fuel switch over, can not therefore , be established without a comprehensive

, integrated simultaneous monitoring of the emissions from both the stacks and other associated process parameters .

Table II-35-1 Coke pulverization Mill Stack (with Fabric Filter) – Cement plant – Pakistan .

**Emission concentrations in mg /N³
(dry gas , 101.3 K Pa and 0 °C) .**

Prameters	Pollutio n Control	Measured Pulverizatio n Mill Stack	Concentration s PH/PC and PH kilns stacks	NEQ S Limit s
Particulate Matter(PM)	ESP /FF	388 -412	55 – 195	500
Oxides of Sulfur(SOx)	None	31 – 1402	0 – 1337	1700
Oxides of Nitrigen(NOx)	None	256 – 816	322 – 629	1200
Carbon monoxide(CO)	None	492 – 1321	156 – 1625	800

ESP Electrostatic precipitator .

FF Fabric Filter

Source : NEQS – Pakistan 2003 .

All the pollutants from pulverization mill stack are within the NEQS limits , except for CO in one case . Except for particulate matter , the order and variation of concentrations of other pollutants from pulverization mill stack are same as for kiln stack , pointing towards the same origins of these emissions . Higher particulate matter concentrations from coke

pulverization mills may due to suboptimal operation of the installed fabric or the increased input loads from the mill .

II-36 Spontaneous coke fires :

One potential hazard of the coke depending upon its characteristics and ambient conditions , is its propensity to spontaneous ignition and combustion at rather low temperatures , which leads to outbreak of fire in stored coke . This spontaneous combustion may occur naturally or the combustion process may be triggered by other causes , like lightening , electric or other mechanical sparks .

Three necessary elements of fire triangle , which must occur simultaneously to cause a fire are fuel , heat and oxygen . Removing any one of these requirements would prevent fire .

Coke reacts with atmospheric oxygen even at ambient temperatures and this reaction is exothermic . If the heat liberated during the process is allowed to accumulate , the rate of the above reaction increases exponentially and there is a further rise in temperature . When this temperature reaches the ignition temperature of coke , the coke starts to burn .

For conditions favoring spontaneous combustion the air supply to be high to enough to support the oxidation , but too small for a sufficient cooling . The temperature , at which the coke oxidation reaction becomes self – sustaining and at which spontaneous combustion occurs , varies depending on the type (nature and rank) of coke and surrounding conditions of heat

dissipation . In poor quality coke and where the heat retention is

high the coke and carbonaceous material may start burning at temperatures as low as 30 – 40 °C. Besides burning away the important nonrenewable energy resource and causing financial losses , these fires pose danger to man and machine , raise the temperature of the area , and may cause damage to the adjacent buildings and structures . Excessive levels of air pollution of the occupational and surrounding atmosphere would result from such fires , for as long as the fire continues .

II-37 Coke dust explosions:

In cement kiln coke is used in pulverized form . Pulverized coke is potentially explosive and can be set off by spontaneous ignition or by proximity of hot elements , static charges or flames . Pulverized coke is present in the coke pulverization mill and in the elements of the coke feeding and firing system . Like fire triangle, there is explosion pentagon of five necessary elements of fuel , heat , oxygen , suspension and confinement which must occur simultaneous , to cause and propagate an explosion . Like the fire triangle , removing any one of those requirements would prevent an explosion from propagating . For example , if fuel , heat , oxygen , and confinement occurred together in proper quantities , an explosion would still not possible without the suspension of the fuel . However in the this case a fire color occur . If the

burning fuel were then placed in suspension by a sudden blast of air , all five sides of the explosion pentagon would be satisfied and explosion would be imminent .

The principal impact of any coke dust explosion is consequent potential loss of the human life and limb .

Other major impacts include loss of fuel , destruction of the machinery , equipment and surrounding structures and loss of production due to possible closure of plant for some time .

Socio – Psychological impacts of such an explosion , if it ever occurs unfortunately , on the surrounding communities and the

plant staff itself , owing to their persistent fears in future , and their reaction to such an incidence , may turn out to be more disastrous , than the incidence itself .

II-38 Coke dust impacts on electrical system :

Under all circumstances , coke dust would continuously be present in the occupational atmosphere of the plant . Its entry and accumulated in the electrical panels , equipment and machinery , not duly protected , and on power cables .

II-39 Contamination of soil and ground water :

Open storage of coke on unpaved soil surface , with no proper drainage system , may lead to contamination of soil and ground water particularly , consequent to rainfall . The rain water passing through stacks of coke may leach certain

dissolved organic constituents like phenols and carry them to soil and ground water .

II-40- Noise :

Coke crushers and pulverization mill are two main additional sources of noise pollution , resulting from fuel switch – over to coke .

II-41 Pollution control measures :

II-41-1 Process control optimization for emissions control :

Optimization of the clinker burning process is usually done to reduce the heat consumption , to improve the clinker quality and to increase the life time of the equipment (the refractory lining for example) by stabilizing process parameters . The operating cost of an optimal kiln is usually reduced compared to the non – optimized state .

The savings result from reduced fuel and refractory consumption , lower maintenance cost and higher productivity among other factors .

In order to keep heat losses at minimum , cement kilns shall be operated at lowest reasonable excess oxygen levels . This requires highly uniform and reliable fuel and fuel presentation in a form allowing easy and complete combustion . These conditions are generally fulfilled by all liquid and gaseous fuels . For pulverized solid fuels including petcoke , good design and proper operation of the feeding system is essential to

meet these conditions . Further optimization include measures like homogenizing the raw material and improving the clinker cooler operation .

Reduction of emissions such as particulate matter , SO_2 , NO_x , and CO is essential secondary effect of this optimization . Smooth and stable kiln operation close to design values of process parameters tends to reduce all kiln emissions .

II-41-2 Particulate Matter emissions control :

Following are the main sources and operations , which are resulting into additional emissions of particulate , consequent to switch over from fuel oil to coke in cement production .

II-41-3 Control of PM emissions from kilns and coke pulverization mills :

Continued use of electrostatic precipitators or fabric filters on kiln systems as well as coke pulverization mills , shall be necessary to control PM emissions and keep them well within reasonable limits .

a- Electrostatic Precipitator (EP) :

Electrostatic precipitators generate an electrostatic field across the path of particulate matter in the air stream . The particles becomes negatively charged and migrate towards positively charged collection plates . The collection plates are rapped or vibrated periodically , dislodging the material so that it falls into collection hoopers below . It is important that EP rapping cycles

are optimized to minimize particulate re – entrainment . EPs are characterized by their ability to operate under conditions of high temperatures (up to approximately 400 °C) and high humidity . Besides dust , the EP also removes substances that adsorb to the dust particles , such as dioxins and metals if present .

Factors affecting particle removal efficiency of EP are flue gas flow rate , strength of the electric field , particulate loading rate , SO₂ concentration , moisture content and shape and area of the electrodes .

During special conditions such as high CO concentration , kiln start – up , kiln shut down or switching from compared operation (raw mill on) to direct operation (raw mill off) the efficiency of EPs can be significantly reduced .

Control of CO levels is critical in cement kilns when EPs are used to for particulate abatement , to ensure concentration are kept well below the lower explosive limit . If the level of CO in the EP rises (typically to 0.5 % by volume) then the electrical system is tripped off to eliminate the risk of explosion . This leads to unabated particulate releases from the kiln . CO trips can be caused by unsteady state operation of the combustion system . This occurs more frequently when feeding solids like coke , so solid – fuel feeding systems must be

designed to prevent surges of fuel into the burner . The moisture content of solid fuels is a particularly critical factor in this respect and must be carefully controlled to prevent hold ups or blockages in the fuel preparation and feeding systems .

b- Fabric Filter (FF) :

The basic principle of fabric filtration is to use fabric membrane which is permeable to gas but which will retain the dust . Initially , dust is deposited both on the surface fibers and within the depth of the fabric , but as the surface layer builds up the dust itself becomes the dominating filter medium . Gas for treatment can flow either from the inside of the bag outwards or vice versa . As the dust cake thickness , the resistance to gas flow increases . Periodic cleaning of the filter medium is therefore necessary to control the gas pressure drop across the filter . The most common cleaning methods include reverse air flow , mechanical shaking , vibration and compressed air pulsing . The fabric filter should have multiple compartments , which can be individually isolated in case of bag failure , and it should be sufficient of these to allow adequate performance to be maintained if a compartment is taken off line .

High temperature applications will result in the need for more exotic fabric types than are normally supplied . However a good range of these is available .

Fabric filters therefore have a higher overall efficiency if they are well maintained and filter bags are replaced periodically . A disadvantage of fabric filters is that used filter bags need be wasted . Generally they require more maintenance as compared to EP

II-41-4 SO_x emissions control :

The main sources resulting into additional emissions of SO_x production , consequent to switch over from fuel oil to coke for cement production , are kiln stack and pulverization stack .

II-41-5 Wet scrubber :

The scrubber is the commonly used technique for flue gas de – sulfurization in coke – fired power plants . The SO_x is absorbed by a liquid / slurry sprayed in a spray tower or is bubbled through the liquid / slurry . The absorbent can be calcium carbonate , hydroxide or oxide . The slurry is sprayed in counter current to the exhaust gas .

In case of cement , the spent slurry may be collected in a recycle tank at the bottom of the scrubber , where formed sulfate can oxidized with air to form calcium sulfate di – hydrated .

The di – hydrated can be separated and used as gypsum in cement milling .

The wet scrubber also significantly reduce the HCL , residual dust , metal and NH₃ emissions . A wet scrubber can be fitted to all types of kilns .

II-41-6 Activated carbon adsorption :

Pollutants such as SO₂ , organic compounds , metals , NH₃ , NH₄ compounds , HCL and HF may be removed from the exhaust gases by adsorption on activated carbon is periodically extracted to a separate silo and replaced with fresh adsorbent . By using the exhausted activated carbon in the kiln , the trapped substances are returned to the system and to a large extent become fixed in the cement clinker .

An activated carbon filter can be fitted to all dry kiln systems .

II-41-7 NO_x emissions control :

Two main sources , resulting into differential emissions of NO_x , consequent to switch over from fuel oil to coke for cement production , are kiln system and coke pulverization mill .

There is no significant difference between maximum concentrations , resulting from coke and fuel oil .

In most cases , therefore no end – of – pipe treatment would be required . Many cement plants in the world have achieved reduction in NO_x emissions by means of adopting

general primary optimization measures such as process control , improved firing technique , optimized cooler connections and fuel selection .

CHAPTER III

MATERIALS AND METHOD

III-1 Materials :

III-1-1 Petroleum coke :

Two samples of petcoke were used in this investigation .

- i) Sample (1) from Elsiwez refinery – Egypt .
- ii) Sample (2) from Homs refinery – Syria .

III-1-2 Lime stone :

A sample of limestone brought from Atbara Cement Company , was ground and prepared for the test .

III-2 Methods :

The two samples of petcoke were ground , screened and prepared for the test .

III-2-1 Screen analysis of petroleum coke :

The samples were ground by laboratory mill , and screen sieve analysis is done to the samples in different 4 particles.

III-2-2 Determination of sulfur in petcoke :

The percentage of sulfur in petcoke is determined by Eshka Method which proceeds as follow :

- 1- Weigh accurately 1.0 gm of the finely ground coke in a porcelain crucible .
- 2- Mix with 3.0 gm Eshka mixture (2 parts by weight of calcined MgO and 1 part by weight of anhydrous Na_2CO_3 and cover the content of the crucible with one gram more of the mixture .
- 3- Heat the uncovered crucible in an electric furnace for 1 – 2 hours , first gently to expel volatile matter and then at red heat .
- 4- Continue heating till all black particles disappear from the crucible .
- 5- Stir the mass in the crucible during final heating with a stout platinum or nickel wire to ensure complete incineration .
- 6- When incineration is complete (which is shown by the absence of black particles in the residue) cool the charge and transfer it to a beaker .
- 7- Wash the crucible with hot water and dilute the beaker to about 150 ml .
- 8- Add 10 ml of bromine water in the beaker and stand it on a water – bath for half an hour to completely oxidize the sulfur compounds to the sulfate form .
- 9- Add sufficient hydrochloric acid to dissolve the solid matter.

- 10 – Boil the solution to expel bromine and filter .
- 11- Boil the filtrate . Neutralize it with NaOH using 2 – 3 drops of methyle orange as an indicator and add 2 ml of conc. HCL without interrupting the boiling .
- 12 – Run 10 ml of 10 % solution of barium chloride in a fine stream into the boiling solution and continue boiling for 15 minute more .
- 13 – Allow the solution to stand for at least 4 hours , and then filter through a weighed Goash crucible .
- 14 – Wash the precipitator at least 10 time with hot water .
- 15 – Heat the crucible gradually to dull red in an electric muffle furnace .
- 16 – Coal in a disicator and weigh .
- 17 – From the weight of BaSO_4 , calculate the percentage of sulfur in the sample .

III-2-3 Plotting of the results :

The experimental work results were plotted in graphs by using Excell computer programm .

CHAPTER IV

RESULTS AND DICUSSION

IV-1 Screen analysis of petroleum coke :

Screening is a method of separating particles according to size alone . In industrial screening the solids are dropped on , or thrown against a screening surface .

The undersize or fines pass through the screening openings , oversize or tails do not . A single screen can make but a single separation into two fractions . These are called undersized fractions , because although either the upper or lower limit of the particle sizes they contain is known , the other limit is unknown (M/C Smith 2000) .

Materials passed through a series of screens of different sizes are separated into fractions , i.e fractions in which both the maximum and minimum particle sizes are known . Screening is occasionally done wet but much more commonly dry .

IV-2 Effect of Particle Size on percentage Weight passed

(Sample – 1 - Elsiwez Refinery – Egypt)

The obtained results as shown in figure IV-2-1 show the size distribution , it is obvious that increase of particle size lead to increase in the weight passed , which is confarmity with the results of Ibrahim (1991) , it is found that we have similar result , and this obviously due to attrition and fragmentation .

Figure IV-2-1 Particle Size vs Weeight passed (sample-1- Elsiwez Refinery -Egypt)

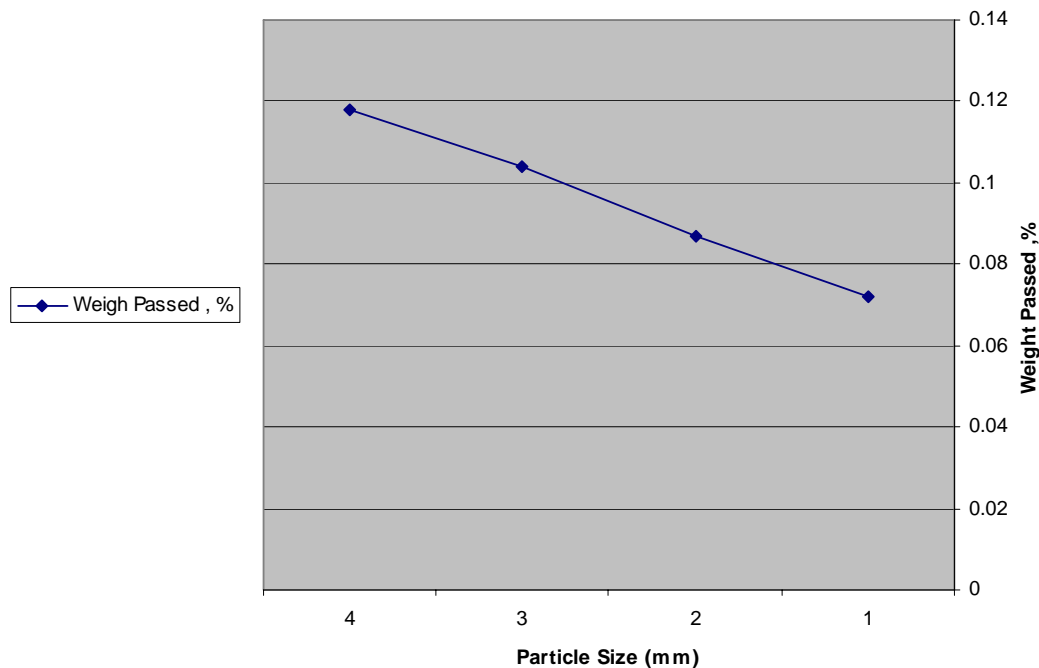
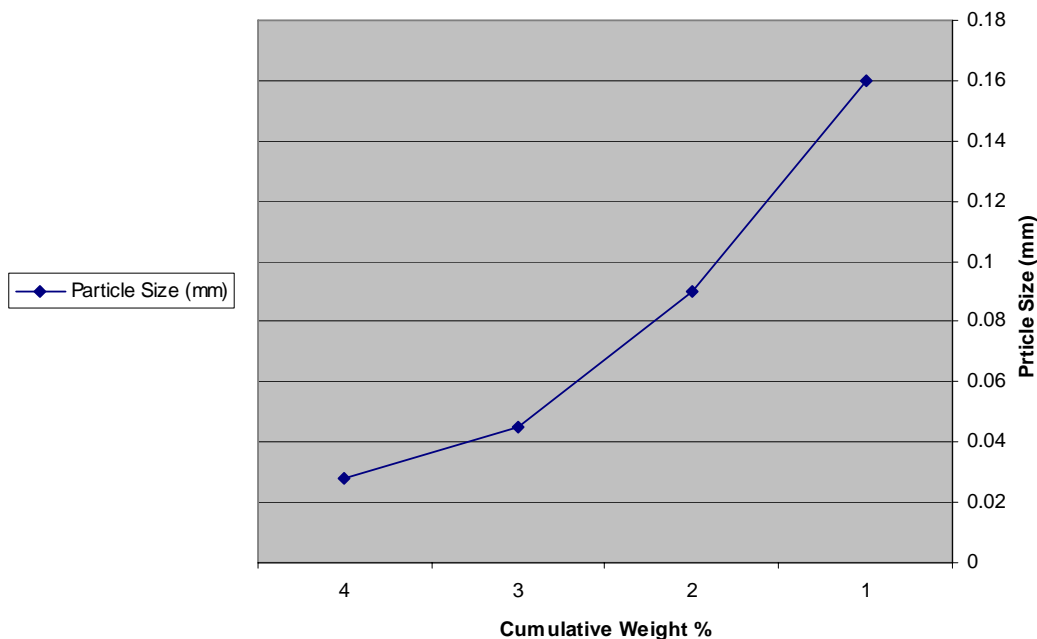


Figure IV-2-1 Particle Size vs Weight Passed , %**(Sample -1 – Elsiwez Refinery – Egypt)****IV-3 Effect of particle Size on percentage cumulative weight passed :**

The obtained results of cumulative screen analysis as shown in figure IV-3-1 show that the increase of particle size lead to decrease in the cumulative weight percent , this is in agreement with the results given by Ibrahim (1991) .

Figure IV-3-1 Cumulative Weight % vs Particle Size(sample-1 -Elsiwez Refinery - Egypt)



**Figure IV-3-1 Cumulative Weight vs Particle Size
(Sample -1 Elsiwez Refinery – Egypt**

IV-4 Effect of particle size on percentage Ash content

∴

The obtained results as shown in figure IV-4-1 show that the increase of particle size lead to increase in the percentage of ash content , so fine grinding for coke is necessary to reduce ash content and to avoid incomplete burning .

Figure IV-4-1 Particle Size vs % Ash content (sample-1- Elsiwez Refinery - Egypt)

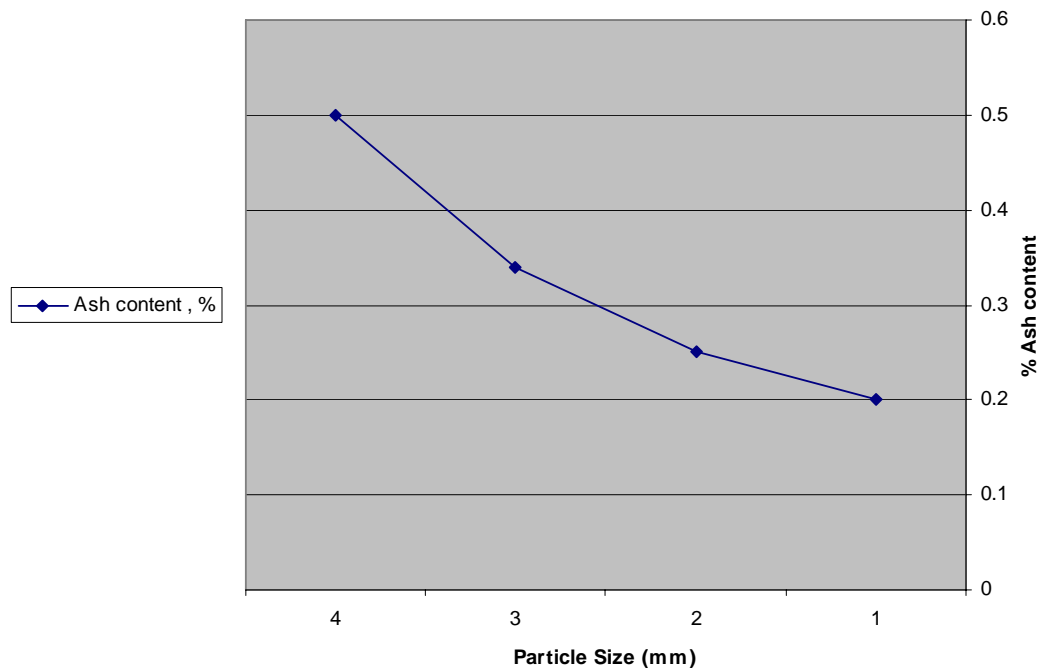


Figure IV-4-1 Particle Size vs % Ash content
(Sample -1 – Elsiwez Refinery – Egypt)

IV-5- CaSO_4 formation during petcoke Burning :

However there are considerable drawbacks in using petcoke as a fuel , for example there may be operational problems which cause rings to form at the upper end of cement kiln . These difficulties are mainly due to the high sulfur content of petcoke , which results in an increase of the recirculation of the volatile constituents inside the burning system (World Cement 2001) .

Out of the many suggestions that have been put forward has developed the idea to mix petcoke with a certain proportion of raw meal (limestone) before it is burnt . The main principle behind this idea is that a considerable fraction of the sulfur content of the petcoke will react with the CaCO_3 content of the raw meal , thus forming CaSO_4 . This quantity of CaSO_4 is not likely to decompose , as it will have a chance to be exposed to the high temperatures of the burning zone , since petcoke burning is practically instantaneous . On the contrary , it will hopefully exit the system along with the clinker (World Cement 2001) .

This particular idea seams rather challenging , not only because a high percentage of petcoke may have to be burnt , but also because its application is not likely to significantly affect the production cost of clinker , as the quantity of the raw meal added to the fuel will be subtracted from the feed . It will of course be very difficult , to remove 100 % of the sulfur by using this method , but even a much smaller reduction will be satisfactory , as the sulfur load of the burning system will be considerably reduced with no significant effects on clinker production costs .

IV-6 Addition of lime stone to petcoke :

The sample petcoke (1) is ground and screened in different 4 particle sizes , 0.028 , 0.045 , 0.090 , 0.160 mm .

15 % of limestone is added to the petcoke in order to reduce sulfur in petcoke .

The samples are fired in electric furnace in different temperatures , 600 °C , 900 °C , 1100 °C .

Analysis of limestone used in the experiment brought from Atbara Cement Company as below :

SiO ₂ :	4.20
Al ₂ O ₃ :	1.2
Fe ₂ O ₃ :	0.84
CaO :	52.80
MgO :	0.9
L.O.I :	39.40

Titration : 93.5

Source : Atbara cement factory .

Analysis of petcoke sample used in the experiment :

(sample – 1 – Elsiwez Refinery – Egypt) as Received :

Cube density :	0.966
Analytical Moisture :	1.3
Sulfur , wt % :	5.0 – 5.2
N ₂ – wt % :	1.9 – 2.0

Fixed carbon , wt % :	87
Ash Content , wt % :	0.4
C / H ₂ Ratio :	87.2 / 4.3
Volatile Matter , wt % :	12 – 14.2
Calorific Value :	8500 Kcal / Kg
Grindability Index :	60 – 80

• **Metal content (PPM) :**

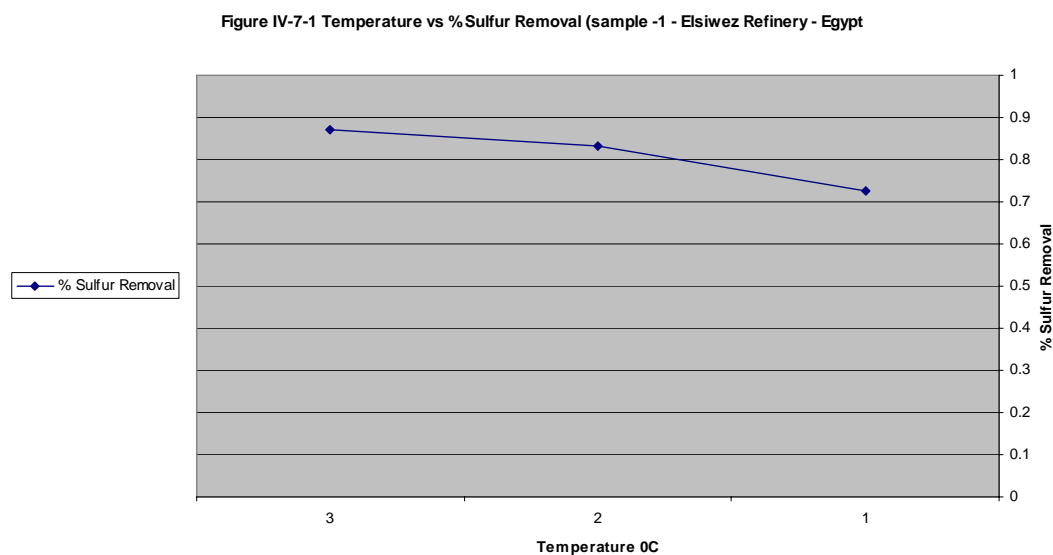
Ca (Calcium) :	110
Cr (Chromium) :	9
Cu (Copper) :	11
Fe (Iron) :	83
Ni (Nickel) :	380
Si (Silicon) :	410
Na (Sodium) :	130
V (Vanadium) :	350 – 500
Mg (Magnesium) :	14
Co (Cobalt) :	0.8
Mo (Molybdenum) :	2.0
Pb (Lead) :	3.0
Ti (Titanium) :	14

Source : Elsiwez Refinery – Egypt .

IV-7- Effect of temperature on removal of sulfur :

The obtained results as shown in figure IV-7-1 show that after firing the samples , the increase of temperature increases the percentage of sulfur removal , when comparing this results

with the results given by Ibrahim (1991) , it is found that we have similar results .



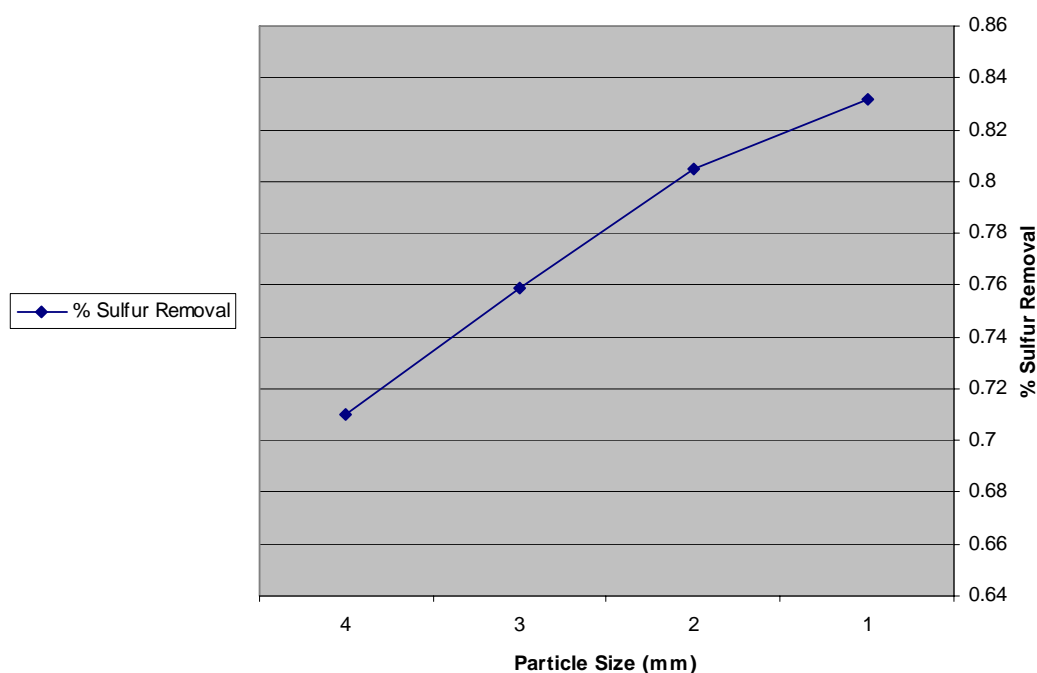
**Figure IV-7-1 Temperature vs % sulfur removal
(Sample – 1 – Elsiwez Refinery - Egypt)**

IV-8 Effect of particle size on removal of sulfur :

The obtained results as shown in figure IV-8-1 show that the low particle size enhances the reduction of sulfur percentage in the sample , because the decrease of particle size leads to

increase in specific area of coke particles , and this may improve both the coefficient of heat and mass transfer , when comparing this results with the results given by Ibrahim (1991) , it is found that we have similar results .

Figure IV-8-1 Particle Size vs % Sulfur Removal (Elsiwez Refinery - Egypt)



**Figure IV-8-1 Particle Size vs % sulfur removal
(Sample – 1 – Elsiwez Refinery – Egypt)**

IV-9 Thermal treatment of petcoke from Homs Refinery – Syria (sample – 2) ;

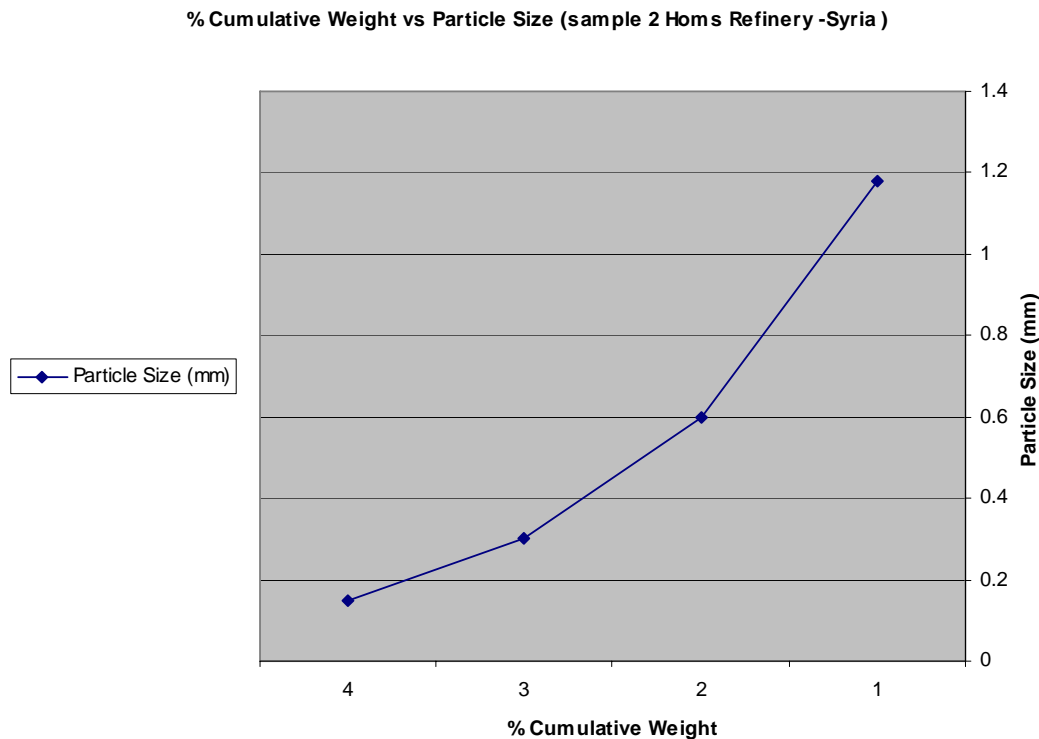
Specifications and analysis of sample is recieved from the refinery in certificate as follows :

Apparent density	:	1.2 – 1.3
True density	:	1.30 – 1.40
Moisture (% wt)	:	4.40 – 5.00
Volatile matter (% wt)	:	6 – 12
Carbon content (% wt)	:	62
Sulfur content (% wt)	:	8.9 – 9.1
Ash content (% wt)	:	0.6 – 0.8
Grindability factor	:	60 – 80
Gross calorific value (Kcal /Kg)	:	8300 – 8400
<u>Metal content (PPM) :</u>		
Vanadium	:	500 Max.
Nickel	:	50 Max.
Molybdenum	:	50Max.
<u>Granules Size PCS (% wt) :</u>		
Less than 1	inch :	75 – 80
From 1-4	inch :	10 – 15
From 4-8	inch :	3 – 6
More than 8	inch :	1 – 2

IV- 10 Effect of particle size on percentage cumulative weight passed

The obtained results as shown in figure 1V-10-1 show that the increase of particle size lead to decrease the cumulative weight passed , comparing this results with the

results given by Ibrahim (1991) , it is found that we have similar results .

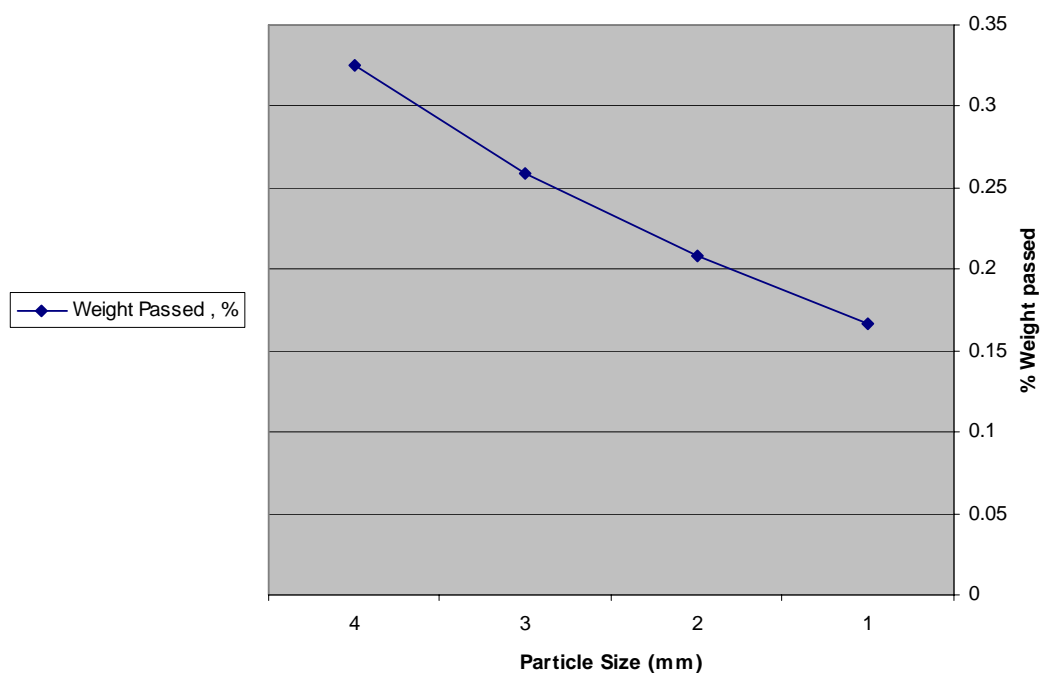


**Figure IV-10 -1 Particle Size vs % cumulative weight
(Sample -2 – Homs Refinery – Syria)**

IV-11 Effect of particle size on percentage weight passed :

The obtained results as shown in figure IV-11-1 show that , the increase of particle size leads to increase in the weight passed through screen , comparing this results given by Ibrahim (1991) , it is found that we have similar results .

Figure IV-11-1 Particle Size vs % Weight passed (sample -2 Homs Refinery - Syria)



**Figure IV-11-1 Particle Size vs Weight Passed , %
(Sample -2 Homs Refinery – Syria)**

IV-12 Effect of particle size on percentage Ash content :

The obtained results as shown in figure IV-12-1 show that the increase of particle size lead to increase in the percentage ash content , comparing this results with the results given by Ibrahim (1991) , it is found that we have similar results .

Figure IV-12-1 Particle Size vs % Ash content (sample -2 Homs Refinery -Syria)

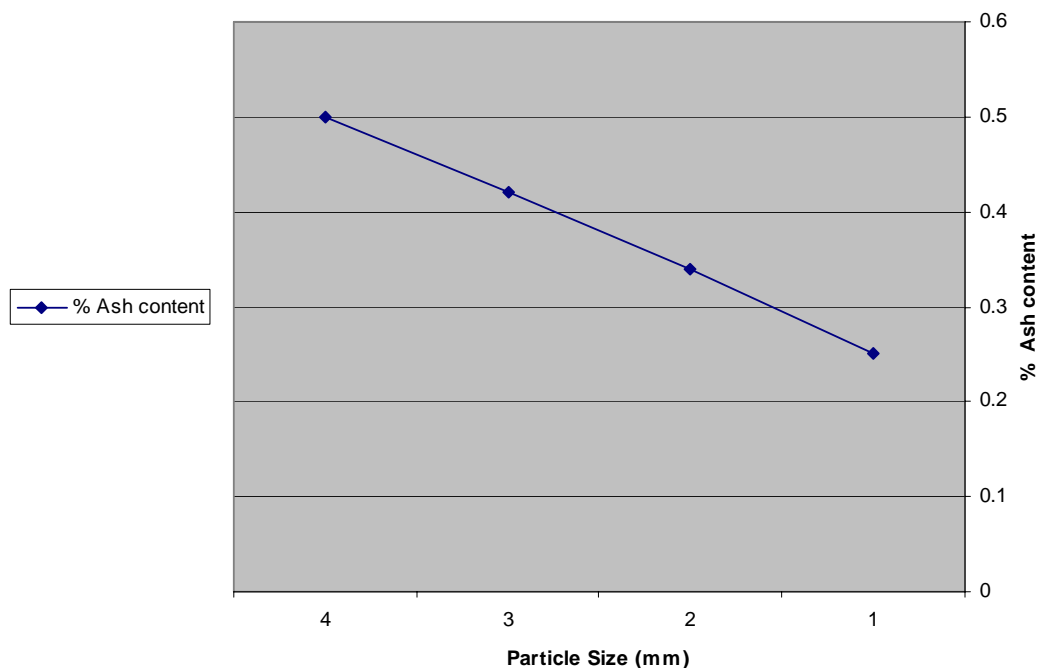


Figure IV-12-1 Particle Size vs % Ash Content
 (Sample – 2 – Homs Refinery – Syria)

IV-13 Addition of lime stone to petcoke (Homs Refinery – Syria – sample – 2 :

The sample of petcoke (2) is ground and screened in different 4 particle size (0.150 ,0.300 , 0.600 , 1.18 mm) .

15 % of limestone is added to petcoke in order to capture sulfur . The samples are fired in an electric furnace in different temperatures , 600 °C, 900 °C ,1100 °C.

The effect of temperature on percentage of sulfur removal as shown in figure IV-13-1 show that the increase of

temperature enhances the percentage of sulfur removal , comparing this results with the results given by Ibrahim (1991) , it is found that we have similar results .

Figure IV -13 -1 Temperature vs % Sulfur Removal (sample -2 -Homs refinery - Syria)

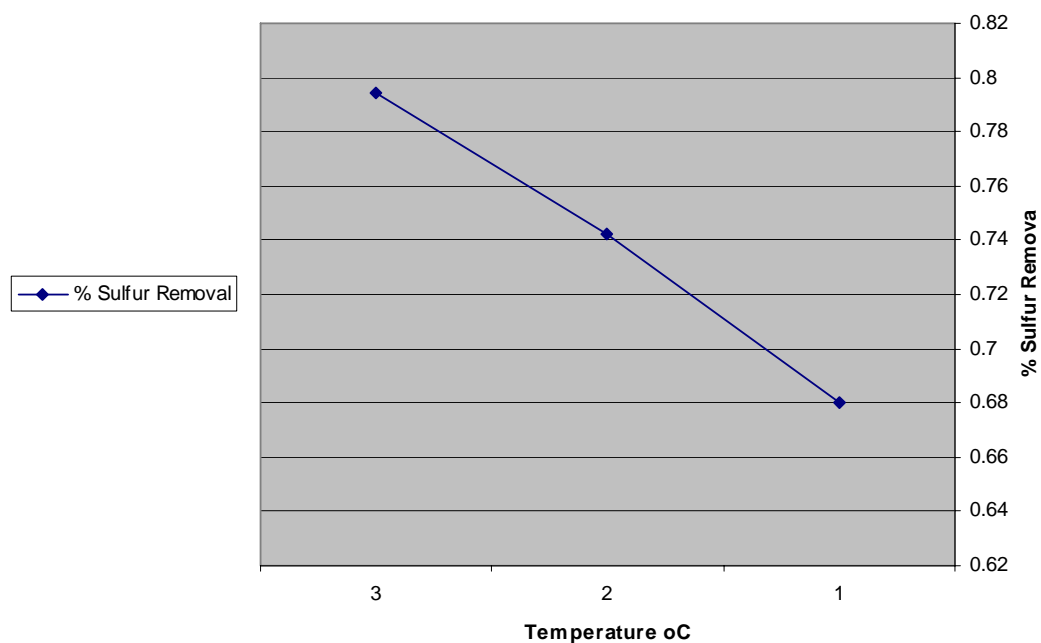


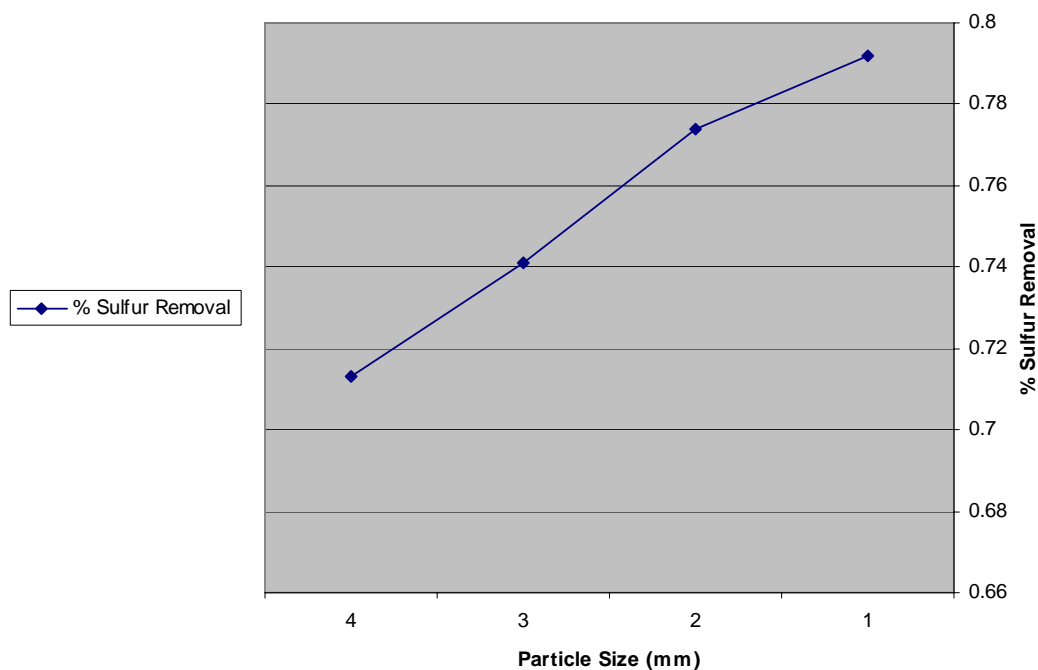
Figure IV-13-1 Temperature vs % Sulfur removal

(Sample -2 – Homs Refinery – Syria)

IV-14 Effect of Particle Size on removal of Sulfur :

The results obtained as shown in figure IV-14-1 show that the low particle size enhances the percentage removal of sulfur , comparing this results with the results given by Ibrahim (1991) , it is found that we have similar results .

Figure IV -14 -1 Particle Size vs % Sulfur Removal (sample -2- Homs Refinery - Syria)



**Figure IV-14 -1 Particle Size vs % Sulfur removal
(Sample – 2 – Homs refinery – Syria)**

The comparison between the two samples treated according to the results can be summarized as follows :

- i- Sample – 1 originally is less sulfur content than sample -2 (5.0 – 5.2 %) to (8.9 – 9.2 %) respectively .
- ii- The percentage of sulfur removal is more in sample -1 than sample -2 , and this confirms the fact that , originally the low sulfur content facilitates the process of sulfur removal .
- iii- The Sudanese petcoke sample showed in the analysis as received a very low sulfur content (< 0.5 %) , and this is a consequent result due to the low percentage sulfur in the original crude .

IV-15 Impact on production costs:

For this purposes , savings in unit cost of production , consequent to fuel switch – over , are determined by taking into account all the main cost factors , affected by this change . Cost components , which shall remain unchanged , have not been accounted for , in this analysis .

IV-16 Basis of analysis :

The analysis is based upon a typical dry process in Atbara Cement Company of total clinker production capacity of 1250 ton /day .

IV-16 -1 Annual production :

Potential annual clinker production of a plant , with clinker production capacity of 1250 ton /day shall be 375,000 tons at 300 days of operation per year .

Since the cost of production is only based on kiln No (3) the design capacity (750 ton /day) an average annual clinker production is 225,000 tons . At common clinker – to cement ratio of 0.95 , corresponding annual cement production is estimated as 245, 000 tons .

IV-16 -2 Capital investment:

The investment costs required to switch from fuel oil to coke normally depend upon the factors like use of imported or local equipment , new or used equipment , extent of standby facilities and design efficacy .

The average capital investment cost for analysis of plant with capacity of 750 tons clinker /day , is taken as \$ 300,000.

(Pillard 2002) .

The cost estimation is based on the following data :

1) Fuel oil consumption :

106 – 108 Kg /ton clinker .

101 – 103 Kg /ton cement .

2) Heat required 1020 – 1040 Kcal /Kg clinker .

3) Production cost of limestone = \$ 4.0

4) Specific power consumption = 130 Kwh /ton cement .

5) Cost of electrical energy = \$ 0.11 / Kwh .

6) Production cost of ton cement = \$ 79 .

Source : Hamza 2005 – ACF.

IV-17 Effected operational costs:

The main changes in operational costs , which would be effected by fuel switch over , are as follows :

a – Direct savings on account of fuel change .

b – Indirect savings on account of added ash contents of coke .

c – Additional Cost of Electricity .

d – Additional cost of Labor .

e – Additional cost of supplies , stores and maintenance .

f – Additional Depreciation cost on account of additional capital investments .

a – Direct Saving on account of fuel change :

– estimated as follows :

Range

One of the benefits of using petcoke as kiln fuel is that after complete combustion , it leaves substantial amounts of ash contents , which become part of the clinker and ultimately of the cement . These added ash contents , thereupon , lead to saving per ton of cement produced , on account of reduction in the cost of raw materials and their processing .

The ash content for petcoke vary from 0.3 – 1.0 % . Taking 0.6 % as average ash content and average coke consumption of 150 Kg per ton of clinker , the average ash addition to the clinker is :

$$0.006 \times 150 = 0.9 \text{ Kg per ton of clinker .}$$

Taking unit production cost of clinker as \$ 30 per ton ,

Saving on account added ash contents work out to be about :

$$\frac{0.9}{1000} \times 30 = \$ \underline{0.02}$$

c – Additional Cost of Electricity :

Unit cost of electricity would increase consequent to fuel switch – over , owing to higher electricity requirement of the coke handling , in – house transport and processing facilities , as compared to the fuel oil . an average increase of 5 % Kh per ton of cement prodused is estimated on this account , ($0.05 \times 130 \times 0.11 = \$ \underline{0.7}$) .

d – Additional Cost of Labor :

Additional manpower would be required for coke handling , in – house transport and processing operations . Ten (10) additional employees , with an average annual salary inclusive of benefits of 480,000 SD per person (40,000 SD per person – monthly), are taken for 750 ton /day plant . Total additional annual salary bill works out to be \$ 18,460 .

Using the annual cement production figure of 245,000 tons ,
the average additional unit cost of labor works out to be about $18,460 / 245,000 = \$ 0.07$ per ton of cement .

e – Additional Cost of Supplies , Stores and Maintenance :

Additional cost of maintenance including supplies and stores of coke handling , in – house transport , processing and firing systems , in place of the fuel oil system , is estimated on the basis of 3 % per annum of the capital investment for fuel switch over . The total average additional annual maintenance cost for average additional capital investment of \$ 300,000 works out to be $0.03 \times 300,000 = \$ 9000$.

Using the annual cement production figure of 245 ,000 tons the average additional unit cost of maintenance works out to be about $9000 / 245,000 = \$ 0.03$.

f – Depreciation Cost on account of Additional capital investments:

Additional annual depreciation cost , on account of the investment made for fuel switch – over , are estimated on the

basis of 5 % per annum of the investment , assuming an average life of 20 years , straight – line relationship for depreciation and zero salvage value . The total average additional depreciation cost , for average additional capital investment of \$ 300 , 000 works out to be : $0.05 \times 300,000 = \$ 15,000$.

Using the annual cement production figure of 245 ,000 tons the average additional unit cost of depreciation works out to be about : $15,000 / 245,000 = \$ 0.06$ per ton of cement .

g – Additional Cost of (15 %) limestone added to petcoke fuel:

Taking 150 Kg fuel as petcoke consumption to produce one ton of clinker :

Average value : 150 Kg fuel /ton clinker .

Consumption of 15 % limestone :

$$0.15 \times 150 = 22.5 \text{ Kg /150 Kg fuel .}$$

Total consumption of limestone for 750 ton clinker /day :

$$\frac{22.5 \times 750}{1000} = 16.8 \text{ ton /day .}$$

$$\text{Cost of 22.5 Kg limestone} = \frac{4}{1000} \times 22.5 = \$ 0.09 .$$

Since the production cost of ton limestone is \$4 .

Table IV-17-1 presents the net difference of unit cost of production (in \$ per ton of cement) , resulting from fuel switch

– over from fuel oil to petcoke , on the basis of values of effected cost variables .

Table IV-17-1 Differences in unit Costs of production (in \$ per ton of cement) on account of Fuel Switch – over from fuel oil to petcoke :

Nature of Cost	Cost Saving (\$ per ton)
1- Direct savings on account of fuel changes	12.9
2- Indirect savings on account of added Ash contents of coke .	0.02
3- Additional cost of Electricity .	0.7
4- Additional cost of Labor .	0.07
5- Additional cost of supplies , stores and maintenance .	0.03
6- Additional depreciation cost on account of additional capital investment .	0.06
7- Additional cost of limestone .	0.09
8- Miscellaneous additional operational cost .	0.1
Net Average Saving (\$ per ton of cement) .	11.87

Net Average Saving = Total Saving Cost – Total additional Cost
 $(12.9 + 0.02) - (0.7 + 0.07 + 0.03 + 0.06 + 0.09 + 0.1)$

Net Average Saving (\$ per ton of cement) :

$$12.92 - 1.05 = \underline{\underline{\$ 11.87 .}}$$

The above analysis shows that the net average savings on production costs would be of the order of \$ 11.87 per ton of cement. Actual savings would however vary from plant to plant and also from time to time , depending upon variations in all the cost effecting factors ,

$$\text{percent Cost Reduction} = \frac{11.87}{12.92} \times 100 = \underline{\underline{15 \% .}}$$

IV-18 Technical Data (Offer Received from Pillard company-(France) – 2002 :

Rotary Kiln :

- Kiln No		3
- process	Type	Dry
- Product	Type	Cement
- Kiln output	TPD	750
- Kiln Diameter	m	100
- Kiln Length	m	100
- Length of burning zone	m	23
- Rotation		acw
- Specific heat consumption	Kcal/Kg	100
- Coolers type		satellite

Fuels :

- Heavy Fuel Oil :

- LHV	Kcal	9600
- Pressure at burner		
- Temperature	°C	140
- Viscosity at burner	Cst	{ 17

Pulverized Fuel :

- Type		Petcoke
- LHV	Kcal/Kg	8500
- Temperature at burner	°C	60
- Residual Moisture Content	% max	1
	148	
- Volatile matter	% wt	8 – 13
- Sulfur Content	% wt	6 – 6.5
- Ash Content	% wt	0.5 – 1.0
Fineness:		
Retained at 90 mm	% wt max	4
Retained at 200 mm	% wt max	1

Utilities :**Electricity Supply**

- For instruments	220 V , 1 Ph , 50 Hz
- For motors	420 V , 3 Ph , 50 Hz
- Motor insulation	IP 54
- Transmitter output	24 V , 4 – 20 m
- Instrument air	
- Pressure	bar g max 7

	bar	g min	5
- Quality			Dry , clean and oil free

Geological Conditions

- Atmosphere		non aggressive
- Altitude	m (ast)	300
- Installation		indoor

Plant Site conditions

- Ambient temperature	°C max	30
	min	10
- Relative humidity	% max	70
	min	30

Specifications

One (1) Rotaflam Rotary Kiln Burner For Petcoke /Oil

Firing :

- Burner output	Gcal/ hr max	4
- Burner hot end length	m	7
- Refractory lining	mm	8
- Total combustion air flow		Nm ³ /hr
5040		
- Primary air flow	Nm ³ /hr	360

- Coal flow rate	Kg/hr max
513	
- Conveying air flow rate	Nm ³ /hr
110	
- Oil flow rate	Kg/hr
416	

Comprising :

- Burner complete with swirl , axial , central primary air streams and coke stream . The outer firing tube hot end is easily replaceable .
- The relative position of each pipe is adjustable so as to be able to modify the tip flow rate of each stream and hence enable flame shaping to suit the kiln (hydraulic jacks are supplied for axial and radial air circuits) .
- Burner tip made out of heat resisting cast iron , and easily replaceable .
- Coke inlet section complete with interchangeable wear insert .
- Throttle valves for swirl /axial /central air adjustment during start – up only , complete with lockage device .
- Air flow measuring element for axial , radial and central primary air amount (loose packing) .
- One (1) central jacket tube for oil gun . Existing one will be reduced .

- One (1) central jacket tube for ignitor .

One (1) Gas Electric Ignitor :

- One (1) gas /electric ignitor complete with :
 - One (1) HT transformer .
 - Two (2) flexible hoses for gas and air .
 - One (1) ionization rod c/w flame relay .
 - One (1) manual isolating valve at gas line inlet .
 - One (1) ignition electrode .
 - One (1) hand operated pressure control valve .
 - One (1) pressure indicator .
 - Two (2) 2 – way safety shut – off valves .
 - One electrical control cubicle including :
 - Circuit breaker on power supply .
 - Two (2) push buttons : Stop and start .
 - Two (2) lights : flame detection and power on .
 - One (1) set of terminal strips for connection of instruments and interfaces .
- **One (1) primary Air Fan :**
 - One (1) primary air fan , centrifugal type , direct driven , static pressure with :
 - One (1) electrical motor with cast iron body :

- installed power	Kw	9
- motor speed	rpm	300
 - One (1) flexible hose (Length = 5 m max) for connection to burner .

- One (1) inlet silencer .

One (1) Telescopic coke connection pipe :

For PF feed to burner :

Average length 4250 mm , adjustment range \pm 750 mm.

The telescopic pipe enables horizontal ,vertical and axial adjustments of burner position without alteration of main coal line connections .

- The pipe length comprises :
 - Two (2) sliding tubes , flanged connections .
 - Seal at outer pipe end to ensure tightness with inner pipe .
 - Two (2) Knuckle joints with seals .
 - C /w flanges and fixing device .

Prices on FOB basis , as per incoterms 2000 from European seaport of Pillard choice , including seaworthy packing .

Item	Designation	FOB basis (Euro)
1-	Rotaflam Rotary Kiln Burner	98,000
2-	Gas Electric Ignitor	9 , 800
3-	Primary Air Fan	45 ,500
4-	Telescopic Fan	7 , 400
5-	Drawings For Existing Trolley adaptation .	5 , 500
6-	Spare Parts For Burner	35 , 200
7-	Three week commissioning	18 , 170

	Total	<u>219 , 517</u>
--	-------	-------------------------

Equivalent to dollars == **\$ 250 ,000 .**

Assume Cost and freight (C&F) is equal to \$ 25,000 .

Assume any miscellaneous cost = \$ 25,000 .

The total Capital investment Cost = **\$ 300,000 .**

CHAPTER V

CONCLUSION AND RECOMMENDATIONS

V-1 Conclusion:

Many methods have been suggested to avoid the operations problems during the use of petcoke , due to its high sulfur content . One of them dectates mixing of the fuel with a small fraction of raw meal , so that CaSO_4 can be formed and exit from the system with the clinker mass , preventing a large fraction of the sulfur load of the fuel from entering the burning system .

A series of experiments were designed and carried out in order to investigate the possible formation of CaSO_4 or similar forms of sulfates directly during petcoke burning . The results of these experiments showed that the formation of such components is possible . The exposure time of these sulfates to high temperature is of critical importance , as they tend to decompose . However, during an industrial application of this method , decomposition problems are not likely to appear extensively ,as the burning time inside the rotary kiln is a matter of seconds .

The results can be concluded in the following points :

- 1- The increase of temperature leads to increase of percentage sulfur removal .
- 2- The low particle Size enhances the percentage sulfur removal in petcoke .
- 3- Low volatile content of petcoke can be compensated by fine grinding to avoid hard burning .
- 4- One of the benefit of using petcoke as kiln fuel is that after complete combustion , it leaves substantial amounts of ash content , which become part of the clinker and ultimately of the cement . These added ash content , thereupon , lead to saving per ton of cement produced ,

account of reduction in the cost of raw materials and their processing .

- 5- The analysis shows that the net average savings on production cost would be of the order of \$ 11.9 per ton of cement . Actual savings would however vary from plant to plant and also from time to time , depending upon variations in all the cost effecting factors .

Range of savings is expected to fall , in most of the cases , in the range of 11.5 – 12.5 \$ per ton of cement equivalent to the percentage of 15 – 17 % .

- 6- The application of this method industrially in cement kiln will appear a percentage of sulfur removal for petcoke more than 90 % because of the high temperature in the burning zone which reaches 1400 °C .

V-2 Recommendations :

- 1- In utilization petcoke as an alternative fuel in cement kiln it should be noticed that after addition of raw meal (limestone) to capture sulfur , the sulfur content does not exceed 1 % .
- 2- Fine grinding of petcoke is necessary to avoid incomplete burning because of low volatile matter content .

- 3- Good storage for petcoke in bunkers to avoid fire explosion .
- 4- Electrostatic precipitator is necessary to reduce exhaust gases emissions and control air pollution .
- 5- The original low sulfur content in petcoke should be considered to facilitate the capture of sulfur , and it is better to be around 5 % .
- 6- The expansion of petcoke production in Khartoum refinery should be considered to meet the demand in different fields in future particularly in cement kiln , aluminum industry , and power generation in circulated fluidized bed boiler (CFB) , corresponding to the low sulfur content in the sudanese crude which consequently will yield a low sulfur content petcoke .
- 7- Production of spong coke for the production of carbon anodes suitable for aluminum industry .
- 8- The density of the calcined coke must be considered , it is critical for producing good anodes , the higher the density the more carbon can be incorporated into the anodes and the longer the anode will last .
- 9- The sulfur in the anode must be below 3.5 % to prevent the sulfur from increasing the electrical resistance of the cast iron concentration between the anode and the power rod .

10- Fluid bed boilers for power production are an attractive outlet for fluid coke since this coke does not require grinding or other preparation steps .

Refferences

- Adams , Harry A., “ Basic Principles of Delayed Coking,” Adams Consulting Enterprises , Inc., January 14 , 1994 , pp. 1- 32 .
- Alsop , P.A. “ Cement Plant Operations Handbook for Dry Procees Plants” 2nd Edition , International Cement Review , Dorking , Surrey (UK) July 1998 .
- Conners , J.W., “ Changes in petroleum Coke Quality and Future Prospects ,” Union Oil Company of California , February.12 , 1981

- Court , W.F., “ Hydraulic Decoking of Coke Chambers,” Refiner & Natural Gasoline Manufacturer , Vol. 17, No. 11, November 1983 , A Gulf Publishing Company Publication , pp. 568- 573 .
- D.G. Hammond , L. F. Lampert , C. J Mart , S. F. Massenzio , G. E. Phillips , D. L. Sellards , A. C. Woerner . Exxon Mobile Research
- Ellis , Paul J., Hardin , Edward E., “ How Petroleum Delayed Coke Forms In A Drum ,” Light Metals 1993 , pp. 509- 515 .
- Elliot , John D., “Delayed Coker Design and Operation: Recent Trends and Innovations ,” Foster Wheeler USA Corporation , 1996
- Ellis , Pual J., Bacha , John D., “ Shot Coke,” Light Metals 1996, pp. 477-484 .
- Environmental Protection Agency (EPA) – USA www.epa.gov/ceepo .
- Floyd C. Hamilton , "Rings and Build – ups in cement kilns, International Cement Review , December 1997, pp. 53-62.
- Gamson , Bernard W., “ Reflections,” Great Lakes Carbon Corporation Research and Needle Coke Production , Private Letter , September 15 , 1983 .
- Gang Soon choi, F.P.Glasser " The sulfur cycle in cement kilns : vapor pressures and solid phase stability of the sulfate

phases , cement and concrete research vol. 18 . 1988 pp.367 – 374 .

- Hardin , Edward E., Ellis Paul J., “ Pilot Delayed Coker,”
Light Metals

1992 , pp. 609- 615 .

- Approach to Delayed coke Process improvement and optimization, Harbi , March 2001.

- B.Sc. Chemical Engineering Project (1991) , supervised by
Dr. Ibrahim Hamid , Minia University – Egypt .

- Jakob , Russ R., “ Coke Quality and How to make It,”
Hydrocarbon Processing , September 1971 , pp. 132- 136 .

- Ka'ante , U., Zevenhoren , R., Backman , R. , Hupa , M . “
The impact of alternative fuels on the Cement manufacturing
Pocess” Proceedings of R,2000 Recovery – recycling –
reintegration , Toronto , Canada , June 2000 pp. 1070- 1075 (CD –ROM) .

- Marsh , H., Clavert , C. , Bacha , J., “ Structure and Formation
of Shot Coke – A microscopy Study ,” Journal of Materials
science , March 13 , 1984 , Chapman and Hall Ltd., pp. 289-
302 .

- OSHA , www.osha.gov .

- Peter , C.F., “ Additional Reflections ,” Great Lakes Carbon Corporation , Research and Needle Coke Production , Private Letter , October 14 1983 .
- Purton , Robert M., Ingersoll- Dresser Pump Company , Telephone Conversation , January 1998 .
- Shea , F.L. “ Production of Coke From Petroleum Hydrocarbons ,” U.S. Patent 2,775,549, to Great Lakes Carbon Corporation , December 25,1956
- WORLD CEMENT , August 2001. -

Appendix (1)

Khartoum Refinery – Sudan

Certificate of Quality

Product : petroleum Coke

Source : Khartoum Refinery – Sudan 2005 .

Appendix (2)
A comparative Table For Adar Crude and imported Fuel
Oil Specifications

TEST		<u>RESULT</u>	
		Adar Crude	Imported

		* *	Fuel Oil *
Density @15°C	Kg /L	0.879	0.958
Sulfur Content	Wt %	0.067	3.29
Pour Point	Oc	39	26
Calorific value	BTU/LB	21198.0	18561.2
Kin. Viscosity @ 50°C	Cst	80	166
Water Content	Vol.	0.9 ⁺⁺	0.5 ⁺
Flash Point (closed/open)	°C	60 /75	90
Optimum pre-heating temp.range	°C	75 /85	110 / 120
- Sediment	Wt %		0.1

* Average results of five (5) imported fuel oil .

* * Average result of three (3) crude oil sample .

+ Max. allowed percent .

++ Sediment Content is included .

Source : GPCS 1997.

Appendix (3)
Port Sudan Refinery Limited
Certificate Of Quality

Product : Fuel Oil

Marketer : Abu Gabra Refinery

Date of Sampling : 13.8.1997

	Methods	
	ASTM / OTHERS	
Density at 15 °C	D 1298	869.0 Kg/m ³
Viscosity Kinematic at 100 °C .	D 445	12.32
Sulfur Content	D 1525	0.84 % wt
Pour Point	D 97	48.3 °C
Ash Content	D 482	% wt
Calorific Value Gross (Cal.)	D 240	45.24 MJ/Kg
Flash Point	D 93	73 °C
Water Content	D 95	0.275 % Vol.
Sediment	D 473	0.091 % wt
Neutralization Value	D 974	
Strong Acid Number		MgKOH/gr

Source : Port Sudan Refinery 1997 .

Appendix (4)

Specifications of petroleum coke sample (Homs Refinery – Syria) as recieved

Source : Homs Refinery – Syria 2004 .

